

A review on solar thermal syngas production via redox pair-based water/carbon dioxide splitting thermochemical cycles



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ABSTRACT

The high power density, ease of transportation and storage and many years of development of internal combustion engine technologies have put liquid hydrocarbon fuels at a privileged position in our energy mix. Therefore processes that use renewable energy sources to produce liquid hydrocarbon fuels from H_2O and CO_2 are of crucial importance. Concentrated Solar Power (CSP) can be employed as the only energy source for the renewable production of hydrogen from water either indirectly, e.g. by supplying the electricity for electrolysis, or directly by supplying the necessary heat for thermochemically producing hydrogen. Among the various thermochemical cycles tested so far for CSP-driven hydrogen production via water splitting (WS), those based on redox-pair oxide systems, are directly adaptable to carbon dioxide splitting (CDS) and/or combined CO_2/H_2O splitting for the production of CO or syngas, respectively. The acknowledgement of this fact has recently revived the interest of the scientific community on such technologies. The current article presents the development, evolution and current status of CSP-aided syngas production via such redox-pair-based thermochemical cycles. At first the various redox oxide material compositions tested for water/carbon dioxide splitting are presented and their redox chemistries are discussed. Then the selection of suitable solar reactors is addressed in conjunction with the boundary conditions imposed by the redox systems as well as the heat demands, technical peculiarities and requirements of the cycle steps. The various solar reactor concepts proposed and employed for such reactions and their current status of development are presented. Finally, topics where further work is needed for commercialization of the technology are identified and discussed.

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1. Introduction

Conventional, fossil, liquid hydrocarbon fuels will continue to cover a major portion of the ever-increasing world energy requirements for the foreseeable future, basically due to their demand in transportation and the existing relevant extensive infrastructure. In this perspective, the direct use of non-fossil, Synthetic Liquid Fuels (SLFs) is an intensively pursued alternative. Currently, the term “Synthetic Fuel (synfuel)” refers to a liquid fuel produced at commercial scale from low energy content carbonaceous sources, such as coal, natural gas, oil shale and other biomass, that are upgraded at the expense of additional energy, also obtained from the combustion of fossil fuels [1]. The terms Gas-To-Liquid (GTL) and Coal-To-Liquid (CTL) refer to processes converting natural gas (or other gaseous hydrocarbons) and coal, respectively, into longer-chain liquid hydrocarbons such as gasoline or diesel fuel. In the GTL route, methane-rich gases are converted into SLFs either via direct conversion of methane to methanol in one step, or via syngas as an intermediate.

Syngas is a gas mixture containing varying amounts of CO and H₂ and whose exothermic conversion to fuels has been commercially practiced since a long time ago e.g. via the Fischer–Tropsch (FT) technology [2]. Syngas can be also used as a source of pure hydrogen and carbon monoxide [3,4]. Thus, in fact hydrogen and syngas are the basic raw materials to produce SLFs and chemicals via industrially available processes. These procedures can be rendered more attractive and environmentally friendlier when combined with a renewable energy source, such as solar energy [5]. Indeed, it is generally accepted that only solar-driven technologies offer a permanent solution to both oil independence and climate change due to the unmatched magnitude and availability of solar resource [6]. When solar energy is employed for the production of the raw materials for the synthesis of such fuels, the latter are characterized with the term “solar fuels”. In the broad sense this term can contain in addition to “solar hydrogen”, synthetic liquid hydrocarbons and alcohols produced from reactions between H₂ and CO that have originated from solar-aided dissociation processes as well as metal powders obtained by solar thermal reduction of metal oxides [7].

Fig. 1a (adapted from [6,8]) depicts a partial listing of the various feedstocks and solar energy variances that can be employed to produce such fuels. In this perspective, there are basically three pathways for producing syngas with the aid of solar energy: photochemical/photobiological, thermochemical and electrochemical [9–11]. The first, low-temperature route makes direct use of solar photon energy for photochemical and photobiological processes [11].

The thermochemical route uses solar heat at high temperatures supplied by Concentrated Solar Power (CSP) systems – i.e. special mirror assemblies that track the sun – for performing various high-temperature reactions that produce syngas from transformation of various fossil and non-fossil fuels (Fig. 1b). Such chemical reactions are natural gas steam reforming [12–14], gasification of solid carbonaceous materials like coal or biomass [15–17], or Water Splitting (WS) to hydrogen and oxygen. This last reaction can then be followed either by reaction of H₂ with CO₂ via the Reverse Water–Gas Shift (RWGS) reaction or by reaction of H₂ with CO coming from Carbon Dioxide Splitting (CDS) to CO and O₂, to produce syngas [18,19]. In addition, CSP systems can be employed alternatively to photovoltaics for syngas synthesis indirectly, e.g. by supplying the (solar thermal) electricity for high-temperature electrolysis of steam or of steam/CO₂ mixtures [20,21] according to the third, electrochemical route in Fig. 1a. In the next step, the most promising liquid fuels to be generated from solar syngas are methanol, dimethyl ether (DME) and Fischer–Tropsch diesel [22–24].

Among the thermochemical routes to solar syngas shown in Fig. 1b, solar reforming requires lower temperatures compared to WS/CDS thermochemical processes. However, the latter route employs CO₂ as a reactant. In this perspective lies within the broad, increasing R&D effort on developing effective solutions for reusing and “valorizing” atmospheric CO₂ as a carbon-containing raw material for the production of fuels and chemicals rather than currently treating it as a waste [21]. A review on CSP-aided reforming (dashed line) has been recently published by the present authors [25] whereas CSP-aided coal/biomass steam gasification (dotted line) has been also covered in a series of publications [16,17]. The present work is a review on the activities on CSP-aided syngas production via WS/CDS thermochemical processes (solid line). First, the evolution of thermochemical cycles from WS to CDS is presented. Then the key thermochemistries of the various redox pair materials tested for such applications are delineated, followed by their coupling to relevant solar reactors. In closing, particular issues for future work on the topic are identified and discussed.

2. Redox-pair thermochemical cycles for syngas synthesis: Chemistry issues

The so-called WS thermochemical cycles were proposed initially for the production of hydrogen from the dissociation of water to hydrogen and oxygen. The single-step thermal dissociation of

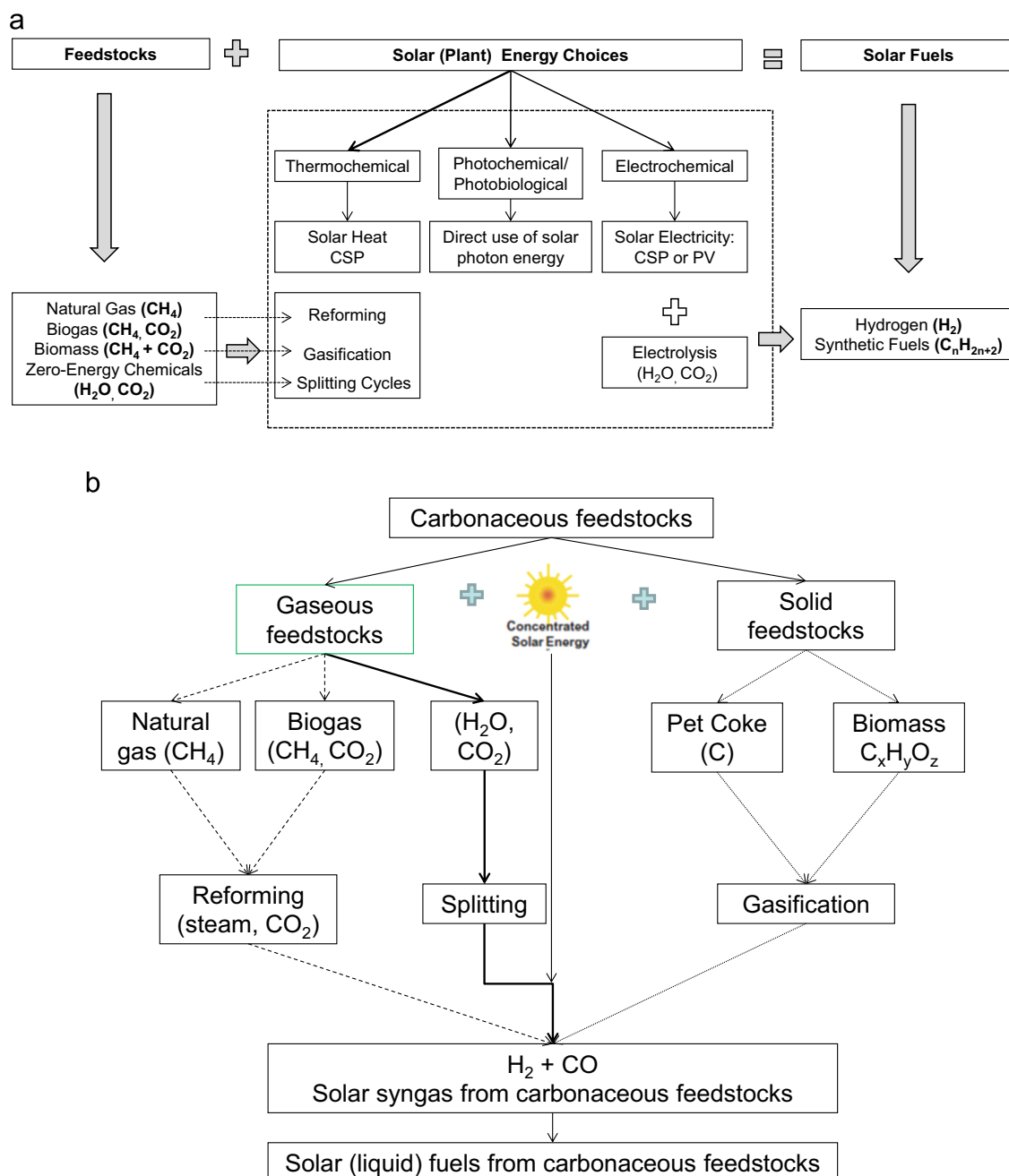


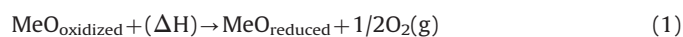
Fig. 1. (a) Partial listing of the various feedstocks and solar energy variances that can be employed to produce solar liquid hydrocarbon fuels (adapted from [6] and [8]); (b) different routes for transformation of various fossil and non-fossil fuels to syngas via high-temperature reactions using solar radiation as the energy source (from [25]).

water (thermolysis) is conceptually the simplest reaction to split water at a first glance. Unfortunately it is impractical due to the very high temperatures needed (above 2500 K) as well as the problem of effectively separating H_2 and O_2 to avoid explosive mixtures. Thermochemical cycles are a series of consecutive chemical reactions (≥ 2), their “net” sum being the splitting of H_2O to H_2 and O_2 . However, the maximum-temperature (endothermic) step takes place at a temperature lower than that of the single-step water decomposition chemical reaction. In this respect, thermochemical cycles by-pass the H_2/O_2 separation problem and further allow operation at moderately high temperatures. Nevertheless, since they involve a highly endothermic step, they need the input of external energy which can be provided by a source of high-temperature process heat.

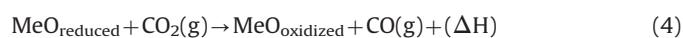
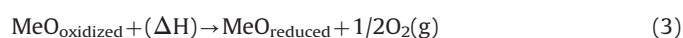
The screening and search of appropriate thermochemical cycles started in the 1960s and the number of theoretical candidates was immense [26]. During the 1970s and early 1980s many studies were carried out to identify the most promising cycles based on different criteria such as thermodynamics, theoretical efficiencies and projected cost [27–30]. In general, most of the development effort during those years was promoted by research institutes and industries from the nuclear energy sector with the intention to diversify the use of thermal energy supplied by nuclear reactors. To this end, the programs developed by the Joint Research Centre of the European Union in Ispra, Italy [30], by General Atomics [31] and Westinghouse in U.S.A. [32] and by the Japanese Atomic Energy Research Institute [33] are worth mentioning. In the late 1980s, the interest in thermochemical cycles decreased drastically.

Until the late 1990s only marginal progress was reported. Mainly two cycles were investigated during that time. The first one was the UT-3 cycle – a 4-step cycle based on the hydrolysis of calcium and iron bromide at 1023 K and 873 K respectively – developed by and named after the University of Tokyo [33]. The other one was the Sulfur–Iodine (SI) 3-step cycle originally proposed and named by General Atomics based on the thermal decomposition of sulfuric acid at 1123 K [34]. A revival in the research and development of thermochemical cycles has taken place in the past few years with the driving force being the production of hydrogen as a greenhouse-gas-free energy carrier to fulfill the requirements of the Kyoto Protocol. In parallel and in contrast to the work conducted 30–40 years ago, concentrated solar radiation has now become more important as a heat source than nuclear heat.

Among the various thermochemical cycles, of particular interest are two-step ones based on oxide redox pair systems. Such cycles operate on the principle of transition between the oxidized (higher-valence, $\text{MeO}_{\text{oxidized}}$) and reduced (lower-valence, $\text{MeO}_{\text{reduced}}$) form of an oxide of a metal exhibiting multiple oxidation states [9,35]. In this concept, during the first, higher-temperature, endothermic step, the higher-valence oxide of such a metal is subjected to Thermal Reduction (TR—reaction (1)), i.e. under the supply of external heat releases a quantity of oxygen and transforms to a lower-valence state. In a subsequent, lower-temperature, exothermic, WS step (reaction (2)) the reduced oxide is oxidized back to the higher-valence state by taking oxygen from water and producing hydrogen. Hence a cyclic operation is established according to the reaction scheme below:



One advantage of the oxide redox pair-based, two-step thermochemical cycles vs. other WS hydrogen production cycles like e.g. the SI one [35] is that the same thermochemical principle can be exploited for CDS as well, for the production of CO according to the following reaction scheme [36]:



The acknowledgement of this flexibility and of the fact that the H_2 produced via reaction (2) and the CO produced via reaction (4) can then be combined leading to syngas, has lead various researchers to propose the above described “solar syngas” production scheme in solar reactors [36]. This “solar syngas” can be further used via the established FT technology to create a number of different product streams including Diesel-like fuel, alcohols and other chemicals. The approach is conceptually simple since the TR step is common for both WS and CDS (reactions (1) and (3), respectively). Therefore a particular redox material and a respective thermochemical reactor can be used for both WS and CDS in one hand separately from each other, i.e. to produce a stream of H_2 and a separate stream of CO. In the other hand the process can be performed simultaneously when steam and CO_2 are co-fed to the redox material, to produce syngas in one step. This generic scheme is depicted in Fig. 2 (adapted from [37,38]).

Obviously, the oxygen yield during the first step (1) or (3) depends on the extent of reduction: the oxidized form of the redox material with the metal cation at its highest valence can be reduced either to a lower-metal-valence oxide or all the way to the respective metal (of zero valence). Highest possible dissociations are in principle sought, since subsequent full replenishment of the oxygen released during dissociation by oxygen taken from $\text{H}_2\text{O}/\text{CO}_2$ during oxidation, results in higher H_2/CO product yields per mass of redox material and thus higher cycle efficiencies. These

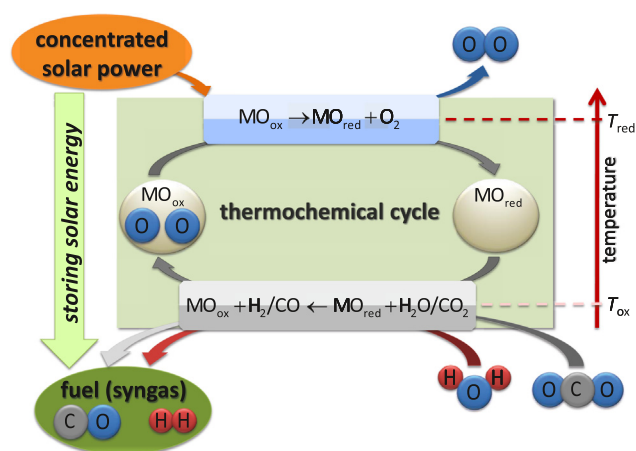
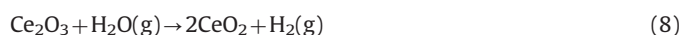


Fig. 2. General schematic of the solar-aided, two-step, redox-oxide-pair-based, water and/or carbon dioxide splitting thermochemical cycle for syngas production (adapted from [37,38]).

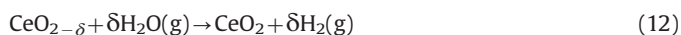
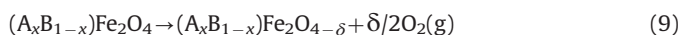
“cycle efficiencies” correlate the higher heating value of the fuel produced to the thermochemical cycle energy input (i.e. the amount of energy that must be supplied to carry out the entire cycle). Hence, both such kinds of systems have been considered for hydrogen/syngas generation via the cycles above: either metal oxide/metal systems (e.g. ZnO/Zn) or metal oxide/metal oxide pairs. Typical examples of the latter case are oxides of a single multivalent metal such as $\text{Fe}_3\text{O}_4/\text{FeO}$, $\text{Mn}_3\text{O}_4/\text{MnO}$ or the more recently tested, $\text{CeO}_2/\text{Ce}_2\text{O}_3$. In these cases, starting from a higher-metal-valence oxide and assuming that all the metal cations change their valence from the higher to the lower number during reduction and vice versa during oxidation, reactions (1) and (2) can be written with the following stoichiometry for e.g. the $\text{Fe}_3\text{O}_4/\text{FeO}$ and $\text{CeO}_2/\text{Ce}_2\text{O}_3$ systems:



The concept of using oxide pairs of multivalent metals for solar-aided thermochemical production of hydrogen via WS first appeared in the literature in 1977 where cycling between $\text{Fe}_3\text{O}_4/\text{FeO}$ (magnetite/wüstite) under the pair of reactions (5) and (6) above was proposed [39]. This proposition introduced the notion of metal oxides as thermochemical reaction media and a new strategy for thermochemical fuel production [40]. The first CSP-aided TR experiments of oxide pairs such as $\text{Fe}_3\text{O}_4/\text{FeO}$ or $\text{Mn}_3\text{O}_4/\text{MnO}$ were performed in the early '80s at the solar furnace facilities of Laboratoire PROCédés, Matériaux et Energie Solaire (PROMES) in Odeillo, France [41–43]. Even though the “proof-of-concept” of the particular process was demonstrated, the temperature needed was higher than the melting points of Fe_3O_4 (1808 K) and FeO (1643 K). This fact resulted in liquid Fe_3O_4 and FeO phases causing a rapid decrease of the iron oxide surface area and thus a deactivation of the material. Therefore research efforts shifted toward alleviating these issues. Indeed, subsequent studies have shown that partial substitution of iron cations in the magnetite's lattice by a transition (e.g. Mn, Co, Ni or Zn), or an alkaline earth (e.g. Mg) metal, forms mixed metal iron oxides of the form $(\text{Fe}_{1-x}\text{M}_x)_3\text{O}_4$ —ferrites. These can be reduced at lower temperatures than the pure magnetite while their reduced mixed wüstite phase $(\text{Fe}_{1-x}\text{M}_x)\text{O}$ is still capable of splitting water [44]. In fact, the idea of exploiting solar-aided thermochemical cycles of ferrites for the decomposition

of CO₂ was proposed as early as 1980 [45] but targeted at that time to producing carbon rather than CO as a source for hydrocarbon fuels. Thermodynamic analysis showed that CO may be thermally decomposed to C and O₂ in a two-step reaction scheme like the above that involves the use of FeO and Fe₃O₄ [46]. Mn(II)-bearing ferrites (Mn_xFe_{3-x}O₄) were employed experimentally for the decomposition of CO₂ to carbon at 573 K [47].

Ferrites belong to the family of spinel materials which, together with perovskites, are two of the most known families of oxides containing multiple metal cations that can exhibit various valence states. Spinel and perovskites are of the general formulae A⁺²B₂⁺³O₄ and A⁺²B⁺⁴O₃, respectively; however, more than one cation of the same valence can occupy the A or B sites, e.g. (A_xB_{1-x})⁺²(C_yD_{2-y})⁺³O₄ and (A_xB_{1-x})⁺²(C_yD_{2-y})⁺⁴O₃ are respective typical formulae with two metal cations at each site. In addition, both single- and multi-metal, multivalent metal oxides such as Fe₃O₄, CeO₂, spinels and perovskites form a wide range of stable, non-stoichiometric compounds, denoted as Fe₃O_{4-δ}, CeO_{2-δ}, AB₂O_{4-δ} and ABO_{3-δ}, respectively. All such non-stoichiometric families can operate in a reaction pair scheme similar to (1)–(2) or (3)–(4) above. Therefore, reactions (5)–(8) are written only schematically in terms of simple binary, line (i.e. stoichiometric) compounds. In reality, they represent much more complex situations like non-stoichiometric phases, solution phases and multicomponent oxide materials [48] like the following schemes (9)–(12) for the same exemplary cases of a mixed ferrite and ceria, respectively:



In most cases for practical purposes, lower TR temperatures are selected to avoid phenomena like melting and/or evaporation of volatile compounds, reactant loss or composition changes, activity reduction or side reactions with the reactor materials. Under these circumstances the TR reactions (5) and (7) above are not thermodynamically spontaneous and do not proceed to completion unless a very low partial pressure of oxygen can be achieved in the maximum practical reduction temperature [49]. Thus in practice, the cycles do not take place under the “theoretical” schemes (5)–(8) but rather like the schemes (9)–(12). In other words, the reduction product does not contain all the reducible metal cations at their lower valence state but only a smaller percentage of them since δ is usually much smaller than 1. This has as a direct result the evolution of much less oxygen during the TR step and the consequent generation of less H₂/CO at the subsequent WS/CDS step. An advantage of this in the other hand, is that one can make use of the percentage of the bivalent metal(s) present in the single/mixed oxide phase and “oscillate” during the redox cycle between the reduced and oxidized structure without causing phase transformations (such as to the lower-valence metal oxide or to the respective metal) that can induce structure disruption.

In general, the course of the research efforts evolves along the following path: often at first thermodynamic calculations are performed to determine potentially attractive redox systems and the respective temperature ranges required. Numerous such studies were performed initially for WS [50–53] and subsequently for CDS [48] on such single-metal oxides that can be reduced either to their lower-valence oxide or to the respective metal such as Fe₃O₄, Mn₃O₄, Co₃O₄, Nb₂O₅, WO₃, MoO₂, SiO₂, SnO₂, In₂O₃, CdO, ZnO and CeO₂. These studies have identified a limited number among these oxides being of practical interest given their window of thermodynamically favorable TR and WS/CDS temperatures. In addition,

such calculations provide the upper limits of expected efficiencies since, in most cases, consider full reduction-oxidation of all metal cations to the lower or higher valence respectively—which is not the case as already pointed out. This issue has been already addressed by the research group of SANDIA National Labs (SNL) Albuquerque, NM, U.S.A. In a recent study they demonstrated that allowing only the ideal, stoichiometric line compound FeO as a potential decomposition product for Fe₃O₄ led to quantitatively inaccurate predictions of Fe₃O₄ decomposition temperature. Therefore, the significance of including solution phases rather than only stoichiometric line compounds in thermodynamic modeling was emphasized [49].

Most problems are associated to the higher-temperature TR step common to both WS and CDS cycles. Thermodynamic calculations have shown that for oxide systems that could be easily thermally reduced under air atmosphere at moderate temperatures (e.g. Co₃O₄/CoO) the hydrogen yields during the hydrolysis step were too low to be of economic interest and for systems exhibiting high hydrogen yields during hydrolysis (e.g. Fe₃O₄/FeO, Nb₂O₅/NbO₂) the temperatures required for TR were above their melting points [53]. Excluding thus the first group of oxides, the solution left is to lower the TR temperatures of the oxides of the second group by reducing the oxygen's partial pressure. Thermodynamic calculations have identified the magnitude of oxygen partial pressure effects on the TR step equilibrium and have shown the prohibitive thermodynamics for performing this step under air atmosphere. In practice, most experimental set-ups and reactors use an inert gas to sweep the oxygen out of the reaction chamber and keep the atmosphere under a low oxygen partial pressure. In this case though, recycling inert gas imposes additional energy penalties to the overall process. An alternative option is to reduce the metal oxide under vacuum total pressures. Indeed, thermodynamic calculations have demonstrated the beneficial effect of reduced pressure on the extent of reduction for a variety of oxides [54,55].

Then, materials identified as promising are synthesized and tested in lab-scale usually in the form of powders, under non-solar-provided heat. Typical temperatures required for the high-temperature step of these cycles to reach full conversion range from 1100 K to 2300 K. Therefore laboratory tests involve WS, CDS or co-splitting to experimentally determine the respective conditions, product yields, long-term materials performance and stability. Such tests are performed either in ThermoGravimetric Analyzers (TGA) or in typical electrically- or Infra-Red (IR)-heated high temperature furnace test rigs, coupled to Mass-Spectrometers (MS) or suitable gas analysis equipment like e.g. CO, CO₂, O₂ analysers. In such rigs the gaseous products can be monitored as a function of cyclic operating temperature and surrounding atmosphere (in addition to the oxides weight change in the case of TGA). In fact, since water requires vaporization to steam whereas room temperature CO₂ is already a gas and can be used directly, much more experimental studies with respect to CDS appear in the recent literature.

3. Two-step water/carbon dioxide splitting thermochemical cycles

Various redox pairs have been initially explored extensively for WS/TR thermochemical cycles; the relevant issues can be found in several review articles [35,56–58]. Investigations among the most promising of them extended recently to include CDS; these are described in more detail below. A classification of such cycles in the literature is to the so-called “non-volatile” and “volatile” cycles according to whether the metal-containing species remain in the condensed state during the entire process or not.

3.1. Volatile cycles

Since the temperatures required for the thermal decomposition reactions are high, they often exceed the boiling temperatures of the reduced species. Thus, “volatile” redox pairs employed in two-step WS cycles commonly exhibit a solid-to-gas phase transition of the other-than-oxygen product (either the metal or the lower-valence oxide) in the reduction step. This phase transition is thermodynamically beneficial for the process, because a high entropy gain is obtained. In the other hand, significant challenges occur due to the recombination of the other-than-oxygen product of the decomposition reaction with oxygen back to the initial reactant in the product gas stream; hence a common problem of all such cycles is how to avoid in practice the recombination of the decomposition products back to the oxidized state of the oxide.

3.1.1. The ZnO/Zn cycle

Among the many metal oxide/metal systems considered for the two-step WS process [59], the ZnO/Zn system is characterized by a combination of favorable thermodynamic properties: “...Zn is sufficiently non-precious to react with water, has low atomic weight and therefore comparatively high energy content per mass being attractive as a transportable energy vector...” [60]. However, the decomposition temperature of ZnO is approximately 2300 K, whereas Zn melts at 692 K and has a boiling point of 1180 K. This system has been studied extensively from the research group at Swiss Federal Institute of Technology/Paul Scherrer Institute (ETH/PSI) Zurich, who have been investigating several chemical aspects of the thermal dissociation of ZnO [61]. While the work originally focused mostly on the application of this cycle for WS and hydrogen generation [62] more recently also investigations on CDS came into play. The group considered thermodynamically the Zn/ZnO and the FeO/Fe₃O₄ (see below) thermochemical cycles using concentrated solar energy and determined maximum theoretical solar-to-chemical energy conversion efficiencies of 39% and 29%, respectively [63]. A recent study [64] employed a second-law thermodynamic analysis to assess the potential of the cycle for syngas production. At 2235 K and 1 bar, where $\Delta G=0$, and for a desired syngas with a molar ratio H₂:CO equal to 2, which is optimal for FT and methanol syntheses, the cycle efficiency reaches 31.5% when heat recuperation is not employed. At 2030 K, cycle efficiencies of up to 52.1% are attainable with a molar ratio of H₂:CO of 2 by recuperating the sensible and latent heat of the hot products exiting the solar reactor and the heat rejected by the reaction of Zn with H₂O/CO₂. The most challenging part of this process is the reduction of ZnO via solar decomposition into Zn and 1/2 O₂. The reaction rate law and Arrhenius parameters for this reaction were derived for the case of directly solar irradiated ZnO pellets [65]. The product mixture needs to be quenched to avoid recombination, with the quenching efficiency being sensitive to the dilution ratio of Zn(g) in an inert gas flow and to the temperature of the surface on which the products are quenched. As a result, the final product leaving the solar thermolysis reactor/quencher, that is, the feed for the oxidation step, generally contains a substantial amount of ZnO observed to be as low as 6 mol% and as high as 85 mol% depending on reaction conditions and inert gas/Zn(g) dilution ratio.

The second step of these cycles involves the oxidation of the elementary metal in H₂O/CO₂ where H₂/CO is generated and the metal oxide is recovered and recycled. This step need not be solar-aided and since the two steps are decoupled, the production of H₂ and/or CO can be carried out on demand and round-the-clock at convenient sites and independent of solar energy availability [66]. Non-solar exothermic oxidation of Zn by H₂O and/or CO₂ to form fuel (H₂ and/or CO) has been investigated [67]. It was shown that

the presence of inert ZnO affects both the oxidation kinetics and the final asymptotic conversion of Zn. The effect of dilution with inert particles on the Zn oxidation was analyzed. The presence of Al₂O₃ diluent had no positive effect on asymptotic conversion of Zn, whereas the presence of solid ZnO diluent generally increased it and made it less affected by CO₂ concentration in the gas phase. At 673 K about 95% of Zn was converted to the product after being diluted with 50 wt% ZnO, resembling the composition of a typical product mixture generated in a solar reactor.

One of the possible concepts of oxidation is bubbling of steam through molten liquid zinc. Laboratory studies on the kinetics and preliminary tests with a novel concept of a hydrolyser indicated that the WS reaction proceeds exothermally at reasonable rates when steam is bubbled through molten Zn at above about 700 K [68]. In principle, the heat liberated could be used in an auto-thermal type of hydrolyser to melt Zn and produce steam. Alternatively, if the H₂ production plant is realized next to the solar plant, molten Zn could be withdrawn from the quencher at 700 K (or higher) and fed directly to the hydrolyser. In the other hand, transportation of solid Zn to the site where H₂ is finally utilized eliminates the need for troublesome storage and transportation of H₂. The technical feasibility of the solar reactor and hydrolyser at an industrial scale also need demonstration [69]. Alternative approaches for the hydrolysis of Zn include aerosol flow reactors that feature in-situ formation and hydrolysis of Zn nanoparticles [70].

3.1.2. The CdO/Cd cycle

This cycle was one of the first ones to be considered [52] with solar reduction experiments of CdO attempted already in the early '80s at the facilities of PROMES, France [43,71], but the work was abandoned. Despite Cd being toxic, recently the cycle was brought back into study by General Atomics and University of Nevada, Las Vegas [72]. The CdO decomposition reaction: CdO → Cd(g) + 1/2O₂ (g) has been demonstrated in the laboratory in the temperature range 1423–1723 K depending on the carrier gas. As with all such systems, quenching has to be implemented to avoid recombination of Cd with O₂ [73]. The cycle is closing with a Cd hydrolysis reaction where H₂ is produced from molten Cd. A fluidized bed reactor was designed for CdO decomposition in integration with a CSP field, but none of the three processes (decomposition, quenching, hydrolysis) has been demonstrated under real-world conditions so far.

3.1.3. The SnO₂/SnO cycle

The group of PROMES has proposed and systematically investigated the SnO₂/SnO cycle. In this cycle the solar-aided TR step consists of the reduction at approximately 1873 K of SnO₂ into gaseous SnO under atmospheric pressure – since its boiling temperature is 1800 K – and O₂ [74]. Then a non-solar exothermic hydrolysis of SnO(s) follows to form H₂ and SnO₂(s) at about 873 K. Therefore it faces the same re-combination problems, with the product consisting of a mixture of SnO and SnO₂ [75]. Quenching devices as well as reduced partial pressure of oxygen were employed to suppress this recombination. In the other hand, the dissociation rate of SnO₂ is high and it is less dependent on the quenching rate than the dissociation rate of ZnO. In addition, SnO reactivity with O₂ was shown to be lower than Zn reactivity in the high temperature dissociation zone [76]. Thus, the solar step encompasses the formation of SnO-rich nanopowders that can be hydrolyzed efficiently in the temperature range of 800–900 K with a H₂ yield over 90%, higher than that of respective Zn nanoparticles (≈ 55%), which however, exhibited a faster hydrolysis rate [77].

This cycle has been studied for CDS as well. Solar-produced SnO-rich nanopowders were re-oxidized separately by H₂O and CO₂ in a TGA apparatus. SnO conversion approaching 90% was reported, while CO₂ reduction required significantly higher temperatures than H₂O reduction for reaching the same conversion. The product in all cases was only SnO₂—formation of elemental carbon was not observed. Parametric studies have shown as a global trend that both the conversion and the reaction rate improved with increasing temperature and the reacting gas mole fraction. However, the SnO disproportionation reaction to Sn and SnO₂ had an influence on the H₂O and CO₂ reduction rates at temperatures above 773 K [78]. The reactivity of tin-based species was studied in order to elucidate the phenomena occurring during its heating and subsequent re-oxidation with H₂O or CO₂ to produce H₂ or CO. Two main types of reactants were considered: SnO nanopowder obtained via solar sublimation and condensation of commercial SnO powder and Sn/SnO₂ nanopowder obtained via disproportionation of nanosized SnO. The reaction rate was quantified via TGA. The reactivity of SnO and Sn/SnO₂ with H₂O was found much higher than that with CO₂ at a given temperature in the range of 823–923 K. The simultaneous splitting of H₂O and CO₂ was not favorable given the higher reactivity of tin species with H₂O than with CO₂; the splitting of CO₂ required significantly higher temperatures (1073 K) to reach complete particle conversion [79].

3.1.4. The GeO₂/GeO cycle

Korean researchers have proposed a cycle based on the GeO₂/GeO redox pair, named with the acronym KIER-4 [80]. The first cycle step is the decomposition of GeO₂ to gaseous GeO and O₂ at approximately 1673–2073 K (since the boiling point of GeO₂ is 1473 K); the second is hydrogen production by hydrolysis of GeO below 1000 K. The argument in favor of this cycle is that the TR temperature of GeO₂ is by about 270 degrees lower than that of SnO₂. Thermodynamic analysis of GeO₂ decomposition and hydrolysis of GeO confirmed the possibility of this cycle. TR of GeO₂ was demonstrated at lab-scale, TGA conditions at about 1773 K, but as with all such cycles, has resulted in Ge and GeO₂ formation through the disproportionation of GeO into Ge and GeO₂ in the quenching zone.

3.2. Non-volatile cycles

Such cycles employ redox pair oxides which remain condensed during the whole process, bypass the recombination issue found for volatile cycles and include today a wide variety of single- as well as multi-metal, multivalent, metal oxide families. The materials aspects have been comparatively presented in recent publications by researchers of the German Aerospace Center/DLR [37] and of the SNL group [81].

Since these material families remain in the solid state throughout the process their physicochemical characteristics such as specific surface area, particle size, intra-particle porosity etc., become important for the realization of the reaction with the gaseous steam/CO₂. Therefore, many studies explored various synthesis techniques to enhance such characteristics. It should be kept in mind however, that the redox materials' issue in thermochemical cycles is not really the production of materials with high surface area, high porosity or enhanced redox properties in their as-synthesized state, but on whether these properties are maintained during the actual operating conditions encountered in a "real" solar-aided operation involving very high temperatures and repeated thermal cycling. Further issues have to do with the "materials' screening" test procedures. A common problem for several studies on synthesis/characterization of such redox pairs is

that the properties of the synthesized materials are often reported after synthesis or post-synthesis annealing conditions much milder than the actual ones during the subsequently performed TR–WS/CDS tests. Therefore it is often not ensured that either any organic additives employed during synthesis have been completely removed or any structural or phase transformations have been completed. Such phenomena are much more pronounced when particles of nanoscale features are thermally reduced and the original as-synthesized morphology eventually vanishes [81,82]. Consequently, it becomes unclear what are really the phases and mechanisms that take place during either TR (especially) or in the reaction of the oxide with steam or CO₂. In fact, TR temperatures reported in some studies for particular compounds, significantly lower than the bulk of the published results with the same material families, should rather be attributed to in-situ reduction by organic species present during the preparation step and not completely removed before the TR/splitting cycle. One way to avoid such ambiguities is before any TR–WS/CDS testing, to pre-calcine the synthesized materials at temperatures higher than those to be encountered in such tests. Another issue has to do with the reduction process itself: in several studies "chemical" rather than thermal reduction tests are employed to screen and comparatively evaluate various oxide materials with respect to their capability of "releasing" oxygen. In several such cases H₂ is employed as a reductant in a procedure similar to what is referred in catalytic studies as "Temperature Programmed Reduction/TPR". However, it is not at all ensured that a chemically-reduced material will exhibit analogous oxygen release performance when being thermally-reduced. In the other hand, it is not "guaranteed" that a material reduced via chemical (i.e. H₂, C, CH₄ etc.) or even thermal reduction will fully replenish its lost oxygen by abstracting it from H₂O or CO₂ in the second step of the cycle. In fact this is not the case, as already shown in many thermodynamic and experimental studies (with the most notable case being the Co₃O₄/CoO system). Thus, for an "objective" screening, materials should be compared under conditions representative of their foreseen full operation under solar-aided cycles i.e. cyclic thermal-only reduction and oxidation with H₂O and/or CO₂.

3.2.1. The ferrites' cycle

A whole series of ferrites has been tested experimentally as well as studied thermodynamically initially for WS, including either only one or two bivalent metal cations in the A site like MnFe₂O₄ [83], ZnFe₂O₄ [84,85], NiFe₂O₄ [86–89], CoFe₂O₄ [90], Ni_{0.5}Mn_{0.5}Fe₂O₄ [44,91], Mn_{0.5}Zn_{0.5}Fe₂O₄ [92] and of other cation stoichiometries [35,49,93,94]. Various ferrite powders synthesis techniques have been pursued from solid, liquid or gaseous precursors, among others co-precipitation [95], aerial oxidation of aqueous suspensions of Fe(II) hydroxide [96,97], sol–gel [98], atomic layer deposition [99,100], combustion synthesis [86,101] and spray pyrolysis [102]. Comparative testing of ferrite powders has identified the temperature ranges recommended for cyclic operation as well as the effects of process parameters on H₂/O₂ yields [86,89,103]. Their TR temperatures are still high ($\approx$ 1600–1700 K)—an important drawback since it can cause significant sintering of the oxide. Attempts to tackle this problem have been realized by supporting the redox reagent on high-temperature—stable ZrO₂ fine particles or supports [82,104,105].

Such testing of iron oxides and ferrites has been recently extended to include CDS as well, either separately [106,107] or simultaneously with WS. The SNL group investigated experimentally iron oxide/yttria-stabilized zirconia (Fe₂O₃/YSZ) materials with respect to WS and CDS [108–110] via temperature-programmed reduction/oxidation in a TGA between 1673 K and 1373 K respectively and in-situ high-temperature X-ray-diffraction

(XRD). Both WS and CDS were demonstrated over multiple temperature swing cycles. It has also been reported that Fe ions dissolved within the YSZ lattice are more “redox-active” than non-dissolved ones leading to higher oxygen yields, with the maximum amount of CO or H₂ produced per cycle attributed to be limited by the solubility limit of Fe in the 8% YSZ. In addition to thermodynamic comparisons between the Zn/ZnO and FeO/Fe₃O₄ systems mentioned above, the ETH/PSI group also performed comparative TGA studies on simultaneous H₂O and CO₂ reduction over the same materials [111]. They reported that during the interface controlled regime for both, Zn and FeO, H₂O exhibited higher reaction rates with the solids compared to CO₂. A strong dependency between the H₂O/CO₂ molar ratio of the input gases and the H₂/CO molar ratio of the product gases over the temperature ranges investigated was found. The research group of PROMES studied co-splitting of H₂O and CO₂ over FeO (produced via solar thermal reduction of Fe₃O₄) in a TGA configuration. They also reported that H₂ production was favored over CO production with the WS reaction being responsible for over 80% of the global FeO conversion [112]. In a recent work by the group of Aerosol and Particle Technology Laboratory (APTL), of CERTH, Thessaloniki, Greece, Ni-ferrite was shown to successfully simultaneously split CO₂ and H₂O under a co-feeding mode of operation to CO and H₂ with a H₂/CO ratio close to 1.40. The two splitting reactions proceeded with nearly the same rate indicating a similar mechanism at the particular experimental conditions tested [113].

With respect to materials composition, the current consensus seems to be that among the many ferrite materials tested for the targeted application, Zn-containing ones exhibit Zn-volatilization problems and Mn-containing ones phase stability problems under air atmosphere at high temperatures [89,101,114–116]. These facts practically leave only NiFe₂O₄ and CoFe₂O₄ (and their combined stoichiometries) as the most “robust” among the ferrites, capable to operate reliably at the real conditions of a solar-aided process.

With respect to reaction mechanisms, TGA experimental data as well as gaseous products profiles from mass-spectrometers of the test rigs, have been employed by many groups for the development of kinetic models and extraction of the kinetic parameters of the reactions [117–119]. It is interesting to note that recent studies from various groups seem to converge in commonly observed “patterns”. Oxidation of ferrites by WS/CDS is much more rapid than their thermal reduction, requiring thus less time for completion. The most interesting trend is that many research groups advocate that their (independent) results cannot be described by a single rate-governing process throughout the duration of an experiment. In order to explain this behavior, the participation in the reactions of perhaps more than one “population” of oxygen storage sites [118] or iron ions [82] or radiation absorption mechanisms [120], as these are evolving, have been suggested.

3.2.2. The ceria cycle

The CeO₂/Ce₂O₃ pair has been extensively used in automotive emissions control as an oxygen storage system due to its capability of oxygen storage/release under oxygen rich/lean conditions, respectively [121]. In fact, the reduced form of ceria, CeO_{2-x} it was first proposed and tested for (non-solar) cyclic H₂O and CO₂ splitting in the early '80s by Japanese researchers in the range 773–973 K [122,123]; in the first of these studies it is mentioned that “...the results...indicate that ...the oxidation (of the reduced form of CeO₂) by water...is much easier than that by carbon dioxide...”. It should be mentioned though, that the reduced form of ceria was obtained via chemical reduction with H₂ and not thermally. It is therefore surprising how the interest on this system for thermochemical cycles was not revived until 2006, when the

group of PROMES has investigated ceria as a redox pair material for both WS and CDS [124]. Dissociation of CeO₂ to Ce₂O₃ was achieved via a solar reactor at pressures of 100–200 mbar and at temperatures higher than 2220 K where CeO₂ was already in the molten state.

Based on the non-stoichiometry of such compounds described above, a research group at California Institute of Technology (Caltech), U.S.A., proposed a similar ceria-based cycle based on its non-stoichiometric reduction (CeO₂→CeO_{2-δ}), not involving melting. They reported a higher activation energy for CO₂ dissociation (to CO and O₂) than for H₂O dissociation [19]. The group of ETH/PSI modeled oxygen non-stoichiometry of several doped cerium oxide-based materials as a function of temperature and O₂ partial pressure [125]. Above 1200 K ceria was found to react more efficiently with H₂O and CO₂ as the dopant concentration is increased. Results from studies of SNL addressing comparatively the thermodynamics of the WS and CDS processes considering CeO₂ as a redox material [18] indicated that at any temperature below ~1800 K, reduction of CO₂ to CO by Ce₂O₃ – the reduced form of CeO₂ according to reaction (7) – is thermodynamically favored. Furthermore, at temperatures greater than 1100 K, CO₂ reduction is more favored than H₂O reduction. Similar efforts were extended to ferrites [126].

Research with ceria has thus shifted toward performing the reduction at temperatures below its melting point. The same group of PROMES studied TR of CeO₂ by TGA in N₂ stream at 1773 K, whereas WS was performed in a separate packed bed reactor between 973 K and 1318 K [127]. The addition of a cationic element M^{y+} into the ceria structure was implemented to favor oxygen ions mobility during reduction. The elements considered were Al, Mn, Fe, Co, Cu, Zn, Zr as well as YSZ. Ceria reduction yielding Ce(III) species was obtained only in the case of Zr and YSZ, whereas Zr addition (up to 50 mol%) was found to improve reduction yield and suppress sublimation of the solid-oxide solution but the material cycling capability was significantly reduced [128]. With respect to the synthesis route, particular “soft chemistry” routes led to materials with porous morphology resistant to thermal treatment and thus not deactivated during cycling [129].

The group of University of Minnesota, U.S.A. is studying the synthesis and exploitation of 3-dimensionally ordered macroporous ceria and ceria-zirconia systems. CeO₂ samples with differing morphologies were evaluated initially for WS and subsequently for CDS under thermochemical cycling conditions. In the latter case, a reduction temperature of ≈1473 K allowed for appreciable fuel production by several of them. It is claimed that in spite of sintering, the macroporous materials retained an interconnected pore network during 55 cycles, providing a 10-fold enhancement in CO productivity and production rate when compared to non-porous CeO₂ [130–132].

A plethora of dopants, basically lanthanides and alkaline earths, has been tested to improve the redox/thermal stability characteristics [38,125,133–136]. A consensus on the beneficial effect of – anyway well-known from automotive emission control catalysts [137,138] – blending of CeO₂ with ZrO₂ with additions of La₂O₃ to induce thermal stability seems to having been established [38,128,139]. However, in terms of doping with other cations, as mentioned in [81] “...in most cases the improvement in thermal reduction relative to undoped ceria is modest, and in some cases H₂ production by WS actually decreases...”.

Ceria offers several benefits for thermochemical cycling over alternative metal oxide systems: oxygen-deficient ceria shows very good reactivity with water and satisfactory H₂ production yield. However, is not without its own set of challenges, the most significant being the high TR temperatures required – higher than those of ferrites – to attain significant reduction efficiency. At such temperatures – higher than 1800 K – in addition to reactor

material compatibility problems to be discussed below – partial sublimation of ceria can occur that gradually decreases the reduction yield [81,127].

3.2.3. The hercynite cycle

Recently, in addition to ferrites, another spinel material family, the (doped) aluminum spinels of the formula $(A_xB_{1-x})^{+2}Al_2^{+3}O_4$ with cations A and B being Fe and/or Cu have been proposed as thermochemical water splitters. The rationale is to exploit the redox effect of iron oxides in conjunction with the thermal stability of aluminum oxides. For instance, Al–Cu ferrites with various Cu/Al/Fe cation ratios have been synthesized and tested [140]; it was reported that such systems exhibited lower TR temperatures than $NiFe_2O_4$ and $ZnFe_2O_4$. A mixed cobalt ferrite–hercynite system ($CoFe_2O_4/FeAl_2O_4$) has been proposed by researchers from the University of Colorado, Boulder, U.S.A., as an effective WS–TR system [141]. The hercynite occurred due to the reaction between $CoFe_2O_4$ and Al_2O_3 (the ferrite was deposited on an Al_2O_3 support) at the elevated temperatures employed during testing of the ferrite in cyclic experiments. In this case the redox pair reactions are as follows:



Very low TR temperatures (reaction (13), 1213–200 K lower than that of $CoFe_2O_4$) have been reported. These were attributed to a reaction between the ferrite and Al_2O_3 resulting in the formation of the stable aluminates $FeAl_2O_4$ and $CoAl_2O_4$, that is thermodynamically more favorable than the formation of solid solutions or vacancies. Additionally, $CoFe_2O_4/Al_2O_3$ was capable of being cycled between 1473 K (TR) and 1273 K (WS) producing significant amounts of H_2 with no obvious changes in H_2 conversion. The studies were extended to CDS where under either 75 or 600 Torr total pressure, a $CoFe_2O_4$ -coated Al_2O_3 material was capable of producing appreciable amounts of CO after TR at a temperature as low as 1633 K with consistent oxidation behavior up to 23 thermal reductions [142]. These TR temperature values are approximately 100–150 K lower than values reported for ferrites or CeO_2 .

3.2.4. The perovskites' cycle

Despite the fact that perovskites are also non-stoichiometric compounds well-known for their reversibility in delivering and picking up oxygen at high temperatures from their applications in fuel cells [143], did not until recently attract significant attention in relation to a redox pair reaction scheme similar to those above for WS/CDS. Thermal dissociation studies of perovskites appeared in the literature only in 2013. The group of ETH/PSI investigated thermodynamically and experimentally Lanthanum–Strontium–Manganates (LSM)/ $La_{1-x}Sr_xMnO_{3-\delta}$ for both WS and CDS [144]. TR results at 1273 K have corroborated the higher O_2 yield of perovskites compared to that of ceria; however perovskites were characterized by incomplete re-oxidation from CO_2 at 1073, 1173 K and 1273 K. A subsequent study from SNL [145] on Lanthanum–Strontium–Aluminates ($La_{1-x}Sr_xMn_yAl_{1-y}O_{3-\delta}$) on WS and CDS reported also much higher reduction extent than ceria, achieved in addition at about 300 K lower temperature, as well as multi-cyclic capability between 1623 K (TR) and 1273 K (WS or CDS). Chinese researchers have tested perovskites of the type $La_{1-x}A_xB_yFe_{1-y}O_{3-\delta}$ ($A=Sr, Ce, B=Co, Mn$) dispersed in three different commercial supports, ZrO_2 , Al_2O_3 and SiO_2 for CDS and reported that the kind of support induced great differences in the reaction performance [146].

3.3. Concepts for shifting the equilibrium of thermal reduction: Oxygen “sinks”

In summary, for most of the non-volatile metal oxides, the TR step is carried out at temperatures 1600–1900 K. Several concepts have been proposed and implemented for continuously extracting oxygen from the reaction products and thus shifting the thermodynamic equilibrium and enabling higher conversions at lower temperatures.

3.3.1. Operation in vacuum

One of the options is to reduce the metal oxide under vacuum total pressures. Such operation is of special interest because it eliminates the need for purge gas, thus simplifying the process and avoiding energy penalties associated with inert gas recycling. Some of the lab-scale experimental efforts under vacuum or reduced oxygen partial pressure have been already reported above. Along this direction, devices such as solar-driven TGAs are being developed, that enable solid reactants to be directly exposed to high-flux solar irradiation provided by a solar simulator, while their weight change is continuously recorded as a function of time and temperature. A first generation of this novel device was built at ETH/PSI to investigate the thermal dissociation of ZnO at atmospheric pressure [147]. Recently, the same device was employed for the study of TR of CeO_2 at 10 mbar [148]. Some small-scale solar reactors operating under vacuum have also been developed; they will be reported on later in the manuscript.

3.3.2. Chemically-aided (carbothermal) reduction

Another option is to substitute the thermal-only reduction of metal oxides with a chemically-aided reduction via carbon-containing species. These well-known carbothermal reduction schemes, i.e. the reaction of an oxide with carbon or natural gas to produce the elementary metal [7], can “substitute” the first step of thermal-only reduction in metal oxide/metal thermochemical cycles under schemes (15) or (16), which can also be solar-aided [149,150]:



The second step in the first case, is, just like before, the hydrolysis of the metal to produce Hydrogen which can be combined with the CO produced from reaction (15), to produce syngas. Due to the extreme conditions regarding temperature and the separation of Zn and O_2 mentioned above, the solar-aided carbothermal reduction of ZnO where a mixture of ZnO and carbon is converted into Zn and CO at temperatures above 1500 K, was pursued alternatively by the ETH/PSI group in cooperation with the Weizmann Institute of Science (WIS), Israel. It is argued that with the use of biomass as a carbon source the technology becomes CO_2 neutral [151,152].

Using natural gas as a reducing agent (reaction (16)) combines in a single process the reduction of metal oxides with the reforming of methane for the co-production of metals and syngas. When referred to hydrogen-only production, these routes constitute the so-called “open-loop thermochemical cycles” [153], since they employ feedstocks additional to water (carbon-containing compounds) that are consumed and not recycled; therefore are thought of as a process option for a transition period leading from fossil fuel-based hydrogen to hydrogen produced only by renewable resources [154].

3.3.3. Oxygen-conducting membranes

Even though perovskites have been only recently considered for operation in a redox-pair thermochemical cycle, they have

been tested instead in a “chemical” reduction water-splitting scheme employed in combination with a Mixed oxygen-Ion and Electron-Conducting Membrane (MIECM) reactor concept. This idea was proposed almost simultaneously and independently by a Greek research group employing ironate compositions of the type $\text{La}_{1-x}\text{Sr}_x\text{M}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ ($\text{M}=\text{Ni}, \text{Co}, \text{Cu}, \text{Cr}$ [155,156]) and a German group employing compositions of the type $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ (BSCF/BSFZ, respectively) [157,158]. This concept is based again on continuously extracting oxygen from the reaction products at high temperatures by MIEC membranes with high oxygen permeability – such as dense perovskite membranes – that can act as oxygen transfer materials when a difference in oxygen concentration is established along their sides. The operating principle is based on a membrane (e.g. a hollow fiber) that separates the reaction chamber in two compartments (e.g. an inner and an outer cylinder). In the one compartment an oxygen-vacancy-containing redox material (i.e. the reduced form of an oxide) reacts with water vapor in order to fill the vacancies with oxygen. This leads to the simultaneous production of hydrogen. The lattice oxygen ions are transported through the membrane to the opposite side, at the other compartment where this approach can be combined with either one of the two approaches just mentioned above. The second compartment can be kept at very low or zero partial pressure of oxygen; thus the transported oxygen ions will desorb to produce gaseous oxygen and oxygen vacancies. Alternatively, an oxidizable compound (CX e.g. methane CH_4) can be fed in this compartment acting as an “oxygen sink” in order to facilitate the membrane regeneration and vacancy creation process. In this respect the two reactions, $\text{H}_2\text{O}/\text{CO}_2$ splitting and CH_4 reforming can be combined in a single reactor, producing simultaneously hydrogen and syngas. This concept, further elaborated in a series of publications [159–163] has the inherent advantage of being isothermal and continuous. However it also requires elevated temperatures (of the order of 1023–1273 K depending on the perovskite’s composition), thus external heating, that can be also in principle implemented via solar energy. In the other hand these temperatures are significantly lower than the TR temperatures of state-of-the art redox oxide materials currently employed at CSP-aided WS like mixed ferrites (≈ 1623 – 1723 K) or ceria (≈ 1723 – 1873 K).

4. Coupling redox chemistry to solar energy: Heat transfer issues

4.1. Solar concentration systems

Once a redox composition system has been selected, the next step is coupling it to solar energy. The first step of a solar-powered process requires the reflection and concentration of direct insolation using collectors/heliostats. Large-scale concentration of solar energy is accomplished at pilot and commercial Solar Thermal Power Plants (STPP) aimed at the production of electricity from the sun’s rays with four kinds of optical configuration systems using movable reflectors (mirrors) that track the sun, namely [164]: Parabolic Trough (PT) collectors, Linear Fresnel (LF) reflectors, power towers – also known as Central Receivers (CR) – and Dish–Engine (DE) systems. These systems provide in the listed order increasingly higher solar concentrations and increasingly higher process temperatures. The solar energy is concentrated on a focal point by the mirrors, providing thus medium-to-high temperature heat. A heat exchanger (receiver) is used, located in the concentration field of the radiation. The receiver is the heart of the energy conversion process: its’ task is to “trap” (absorb) the concentrated solar radiation and transfer it to a Heat Transfer Fluid/HTF (air, water or molten salt) at the highest possible

temperatures. This solar-heated HTF is then used to operate a conventional power cycle (Rankine, Brayton or Stirling) via another heat exchanger where it performs what its name denotes: transfers its heat to water that is heated, evaporated and then superheated. The superheated steam runs a turbine, which drives a generator to produce electricity.

Solar thermochemical applications, employ the same solar concentrating technologies but instead of a “plain” receiver, the concentrated solar radiation is focused on a receiver–reactor where chemical reactions are performed. At this stage the problem is shifted from chemistry issues (discussed above) to heat transfer ones and the issue of a solar reactor type becomes important. In the particular case examined here, since process temperatures of several hundred up to 2300 K are required to drive oxide-based thermochemical cycles, only solar towers and dishes (Fig. 3a) remain as the technology of choice. Furthermore, considering that hydrogen/syngas production plants require a certain size and taking into account the inherent drawbacks and size limitation of solar dishes, most research and development work in this field was concentrated on implementing thermochemical cycles with solar towers. Pre-development tests under “solar” heat are therefore performed progressively in scale, starting by either solar simulator or solar furnace facilities and progressing to solar-tower configurations. The so-called “beam-down” variant in the last case (Fig. 3c), employs a second, hyperboloidal reflector placed at the top of the tower to re-direct sunlight to a receiver–reactor located at ground level [165].

4.2. Solar receiver–reactor concepts

4.2.1. Directly- and indirectly-irradiated receivers

One generic categorization of solar receivers is according to the mechanism of transferring the solar heat to the heat transfer fluid: directly- and indirectly-heated ones. The characteristics of both these receiver kinds have been described in detail in a recent review on solar natural gas reforming by the present authors [25]. Indirectly Irradiated Receivers (IIRs) consist of absorbing surfaces exposed to the concentrated solar radiation, with heat conducted across their walls to the thermal fluid. The simplest examples are conventional tubular receivers that consist of absorbing surfaces exposed to concentrated solar irradiation, in the interior of which the heat transfer fluid (e.g. a gas or a molten salt) is moving in a direction vertical to that of the incident solar radiation. Alternatively, Directly Irradiated Receivers (DIRs) make use of fluid streams or solid particles/structures directly exposed to the concentrated solar radiation; they are also called and “volumetric” receivers since they enable the concentrated solar radiation to penetrate and be absorbed within the entire volume of the absorber. In different designs, the absorber is either a stationary matrix (grid, wire-mesh, foam, honeycomb etc.), or moving (usually solid) particles. In all cases, the solar receiver is designed so that to approach a black body in its capability to trap incident solar radiation by making use of cavities, black-painted tube panels, or volumetric porous absorbers [164]. According to the geometrical configuration, there are basically two design options: external and cavity-type receivers. In a cavity-receiver, the incident concentrated solar radiation enters through a small aperture into a well-insulated enclosure containing the absorber. The multiple reflections among the cavity’s inner walls, result in a blackbody-behavior of the cavity. Consequently, a trade-off between the maximum energy that can be absorbed and the energy that is irradiated back through the aperture has to be made: a larger aperture provides for more sunlight into the receiver/reactor but also allows additional losses from thermal re-radiation [166]. Cavities are constrained angularly in contrast to external receivers that are usually cylindrically shaped. Schematic

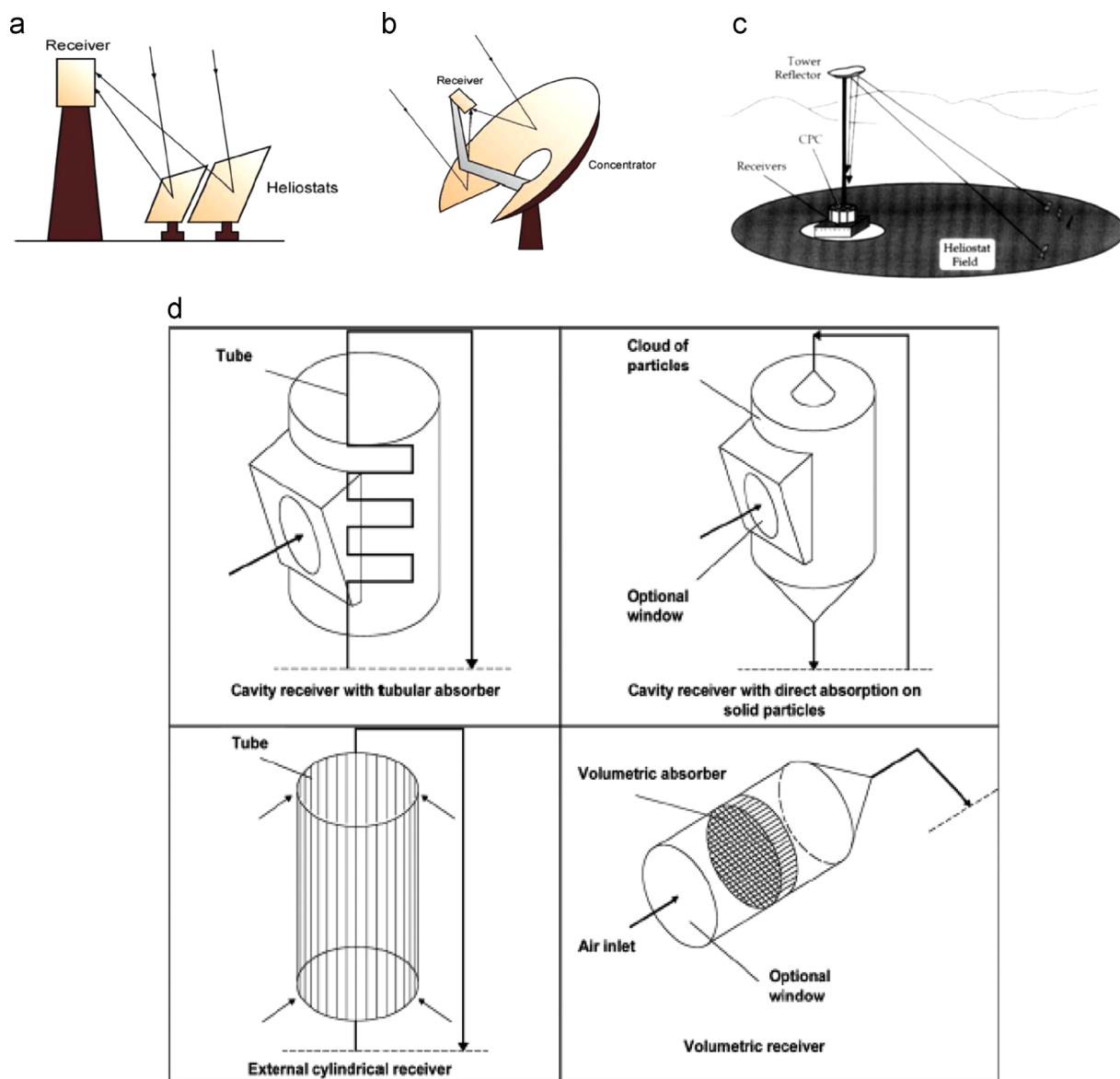


Fig. 3. Schematic of operation of two typical point focusing concentrated solar power systems: (a) solar tower; (b) solar dish, (from [37]); (c) beam-down solar tower receiver (from [165]). (d) Examples of solar receiver configurations: cavity-receiver with tubular panel, cavity-receiver with direct absorption on particle-laden flow, external receiver with tubular panels and volumetric receiver with porous absorber (from [164]).

examples of such configurations of cavity, external, and volumetric receivers are shown in Fig. 3d [164].

4.2.2. “Structured” and “non-structured” reactors

For the efficient design and operation of solar receiver–reactors, concepts from “traditional” chemical reactor engineering should be combined with ways to achieve efficient heating of the reactor via concentrated solar irradiation. The situation in the particular case of redox pairs resembles that of catalytic reactions between gases where the reactant gas species react at the surface of a solid catalyst to be converted to useful gaseous products. In the “traditional” non-solar chemical engineering, such catalytic reactor types can be distinguished in two broad categories depending on whether the catalyst particles are distributed randomly or are “arranged” in space at the reactor level. The first category includes packed and fluidized catalytic beds; the second comprises the so-called “structured” catalytic systems like honeycomb, foam and membrane catalytic reactors, all three of them being free of randomness at the reactor level [167–170].

In a direct analogy to “conventional” catalytic applications, both these configurations can be employed for the solid oxide redox materials. “Loose” particles as well as porous structures can be contained either within solar-heated tubular receivers (IIRs) or being directly exposed to solar irradiation (DIRs). Therefore, both receiver kinds can be “transformed” and adapted to operate as solar chemical receiver–reactors (IIRRs or DIRRs—where the last “R” stands for Reactors) where chemical reactions can take place in an efficient and elegant manner. There are, however, several fundamental differences between “traditional” and “solar” chemical engineering that have to be taken into account. First of all, in the case of DIRRs, in contrast to “traditional chemical engineering” reactors, it is not the hot gases that heat the solid as for example the hot gases from an automobile internal combustion engine heat an initially “colder” catalyst honeycomb in the exhaust. Instead, the solid is solar-heated by absorbing concentrated solar irradiation and then used to heat up the initially colder reactant gases to the reaction temperature. But the most important difference between “traditional chemical engineering” gas–solid catalytic reactions and the gas–solid reactions of the particular system

(s) examined in this work is that the solid reactant (metal oxide) is not a “catalyst” present in much smaller quantities than those of the gaseous reactants, but a reactant itself, with non-negligible mass, that not only has to be heated to the reaction temperature but gets progressively depleted during the course of the reaction, having to be replenished. Therefore it either has to be fed constantly into the reactor if the reactions are to be performed in a continuous-mode, or, alternatively, practical ways have to be “invented” for its in-situ regeneration. In addition, the reactor being either a packed or fluidized bed or a porous structure like a honeycomb or a foam, has to incorporate as much of the redox oxide solid reactant as possible; in one hand to maximize volumetric product yield and in the other hand to avoid the “waste” of external energy in heating chemically-inert materials.

The higher-temperature TR step that needs to be solar-aided requires temperature levels (1600–1900 K, depending on the redox material used) imposing rather challenging reactor operation conditions. Requirements in relation to reactor construction, in particular considering the harsh thermal conditions and chemical atmospheres having to be faced, are superimposed to those for the redox material. The high TR temperatures may cause evaporation of volatile compounds, reactant loss or composition changes, activity reduction or side reactions with the reactor materials. In this context, also solar absorbance and resistance against thermal shock and fatigue must be considered.

4.3. “Temperature swing” operation and heat recuperation issues

Another issue is that the thermal reduction and the ($\text{H}_2\text{O}/\text{CO}_2$) splitting reactions are favored by different conditions [171]. Thermal reduction is thermodynamically favored by high temperatures and low oxygen partial pressures, whereas splitting by low temperatures and high partial pressures of $\text{H}_2\text{O}/\text{CO}_2$. However, the splitting reaction kinetics needs to be considered. To ensure satisfactory reaction rates requires sufficiently high temperatures—but not so high to induce the thermal reduction simultaneously to splitting. Therefore the splitting reactions should, in principle, take place at lower temperature levels (1000–1300 K) than the TR ones. In other words, the complete cyclic operation has to be carried out under a “temperature-swing” mode of about 400 K, whereas in parallel to this, the gaseous feed to the metal oxide has to swing between $\text{H}_2\text{O}/\text{CO}_2$ and inert purge gas. This is a common problem for all single- and mixed-oxide redox systems mentioned above causing complications with respect to both reactor design as well as oxide material handling between the two stages.

This temperature swing induces additional issues relevant to efficient heat utilization between the two reaction steps. The sensible heat available after the higher-temperature TR step has somehow to be recovered and reused effectively. Heat rejection at the TR temperature levels of 1600–1900 K needs to be avoided as far as possible because the associated heat losses can render the efficiency of the system detrimentally low for the economics of the whole process. The importance of such heat recuperation has been extensively stressed [166,172]. Whereas the “materials-related” problem in this respect is the low extent of thermal reduction, in solar-aided operation the heat recuperation which is a property of the reactor design comes also into play. In this respect the various reactors designs proposed and implemented have stemmed from the quest for effective heat recuperation concepts. These concepts are presented below.

5. Solar reactors employed for thermochemical WS/CDS cycles

As mentioned in the Introduction, the initial interest on (water-splitting) thermochemical cycles stemmed from the nuclear

energy sector, with the intention to diversify the use of thermal energy supplied by nuclear reactors. In such a case an indirectly heated TR/WS reactor would be heated “allothermally” i.e. via a de-coupled heated fluid, for example Helium coming from nuclear reactors. However, in the case of solar TR/WS–CDS reactors, the high temperatures required for the TR step practically exclude the use of such “allothermal” reactors where the heating has to come from a solar-heated heat-transfer fluid like air or molten salt. In addition, due to the fact that when using IIRRs, problems relevant to the resistance to heat transfer and the tube materials temperature, limit the actual heat flux to the reaction site (inner region of the tube), there are only few examples of such reactors that have been proposed and employed for both volatile and non-volatile systems.

The majority of reactors are DIRRs that use solid particles or structures directly exposed to the concentrated solar radiation. In these cases, since the working fluid at the TR stage is not air, the receiver–reactors must be equipped with a transparent window, which allows concentrated light to enter the receiver while isolating the working gas from ambient air [173]. The window can also provide for operation under non-atmospheric pressures if needed.

Based on the redox chemistry, we can initially distinguish between two kinds of solar reactors according to the distinction of redox cycles to volatile and non-volatile. The common characteristic of all volatile cycles proposed is that during the TR phase, a gaseous mixture of the reduced phase (this being either an oxide or a metal) and oxygen occurs which needs special treatment to avoid its recombination back to the original oxidized form. This fact precludes the direct combination with the other cycle step, i.e. the “oxidation” (via steam or CO_2) reactor. All such systems therefore consist of two separate reactors: one that performs the TR step from which a condensed reduced phase is obtained together with gaseous oxygen, and a second one where this condensed phase is oxidized (not necessarily solar-aided) and performs the required WS/CDS step. In this respect the cyclic operation can be de-coupled to two stages: one diurnal for thermal reduction and one nocturnal when syngas is produced. Thus solar reactors for such systems have been designed to perform only the higher-temperature TR step. For this reason we decided to include in this category another class of reactors – the so-called “aerosol” reactors – since they are also designed to perform only the TR step, even though addressed to both volatile and non-volatile cycles.

Cycles employing non-volatile redox pairs that remain condensed during the whole process, bypass the recombination issue encountered in volatile cycles. Furthermore, these materials offer more possibilities concerning the reactor concept and process design for the reduction step due to the possible use of either particle receiver–reactors or structured ones consisting of monolithic structures, such as honeycombs, foams or fins. Such reactors are designed to perform both cycle steps but different concepts are implemented for this goal. Based on the categorizations above, an overview of the various solar reactor concepts proposed and tested so far in terms of the redox material configuration (e.g. powder bed, aerosol, shaped object etc.) is summarized in Table 1. The main approaches introduced are described in more detail in the following.

5.1. Solar reactors performing only the thermal reduction step

This category includes all reactors that are designed for materials undergoing volatile cycles as well as “aerosol” reactors. A further distinction can be made with respect to the concept chosen for solar irradiation: direct or indirect.

Table 1
A classification of the various solar reactors proposed for performing water/carbon dioxide splitting thermochemical cycles based on the reactor and heat transfer concepts adopted.

Heat transfer concept	Redox cycle							
	Volatile cycles (only TR cycle step)				Non-volatile cycles (both cycle steps)			
	Reactor concept							
	Non-structured reactors		Structured reactors		Non-structured reactors		Structured reactors	
	Movement							
	Non-moving particles	Moving particles	Non-moving structures	Moving structures	Non-moving particles	Moving particles	Non-moving structures	Moving structures
Directly-irradiated		Rotating cavities Entrained beds Aerosols	Sintered plates	Moving fronts	Packed beds	Spouted beds Moving beds	Honeycombs Foams	Rotary cylinders Rotating fins
Indirectly-irradiated					Packed beds			

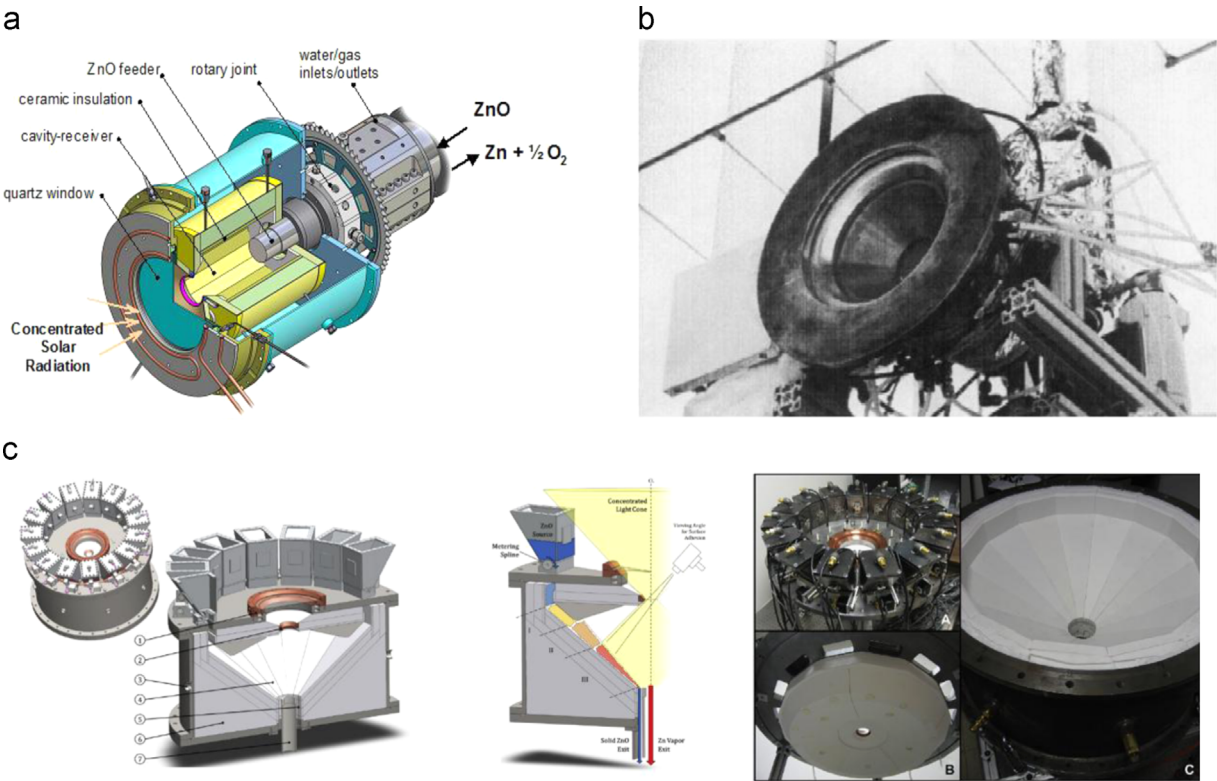


Fig. 4. Cavity solar reactors built by ETH/PSI: (a) schematic of the operation principle of the rotating cavity reactor for the thermal reduction of ZnO (from [174]); (b) first such 10 kW solar reactor prototype tested at PSI's high-flux solar furnace (from [175]); (c) the gravity-fed moving-bed reactor: schematics of operation principle, a single-tile section and actual photographs (from [178]).

5.1.1. Directly-irradiated receiver-reactors

5.1.1.1. The rotating kiln (cavity) reactor. The operation concept of such a solar chemical reactor proposed by the ETH/PSI group for the dissociation of ZnO is shown in Fig. 4a [174]. This windowed rotating cavity-receiver-reactor concept (initially called therefore ROCA reactor [175]), was implemented, developed and tested by the same group in their solar furnace facility. The reactor is lined with ZnO particles that are continuously fed via a screw feeder, held by centrifugal force and are directly exposed to high-flux solar irradiation serving simultaneously the functions of radiant absorber, thermal insulator and chemical reactant. Solar tests carried out with a 10 kW prototype (Fig. 4b) at temperatures

above 2000 K under peak solar concentration ratios exceeding 4000 suns proved the low thermal inertia of the reactor system, its resistance to thermal shocks and the functionality of the overall engineering design [61]. This process is currently being demonstrated at the Megawatt Solar Furnace at the PROMES research facility in Odeillo, France. In this context, a 100 kW solar pilot reactor for the thermal dissociation of ZnO has been designed. Testing campaigns have been carried out in 2012 and 2013. During those campaigns the solar reactor was operated at temperatures up to 1936 K, yielding a Zn molar fraction of the condensed products in the range 12–49% that was largely dependent on the flow rate of Ar injected to quench the

evolving gaseous products [176]. A comprehensive overview of the work to date on the two-step solar H_2O and/or CO_2 splitting thermochemical cycles with Zn/ZnO redox reactions to produce H_2 and/or CO has been recently published outlining the underlying science and the technological advances in solar reactor engineering along with life cycle and economic analyses [174].

The same reactor configuration has been employed by the PROMES group for ZnO thermal reduction under controlled atmosphere at reduced pressure applied by a vacuum pump [177]. The reactant oxide powder is injected continuously inside the cavity and the produced particles are recovered in a downstream ceramic filter. Dilution/quenching of the product gases with a neutral gas yielded Zn nanoparticles by condensation. The solar thermal dissociation of ZnO was experimentally achieved, the reaction

yields quantified and a first solar reactor concept qualified. The maximum yield of particles recovery in the filter was 21% and the dissociation yield up to 87%.

5.1.1.2. The gravity-fed, entrained-bed reactor. Realizing the engineering complexities introduced via the use and maintenance of a rotating reactor assembly, the ETH/PSI group in cooperation with University of Delaware, U.S.A., introduced recently another type of cavity reactor, the so-called gravity-fed, entrained bed reactor [178]. In this implementation, the cavity arrangement is maintained to achieve the high temperatures required for ZnO dissociation. However, the issues of proper solid reactant dispersion and achievement of sufficient residence time for reaction have been

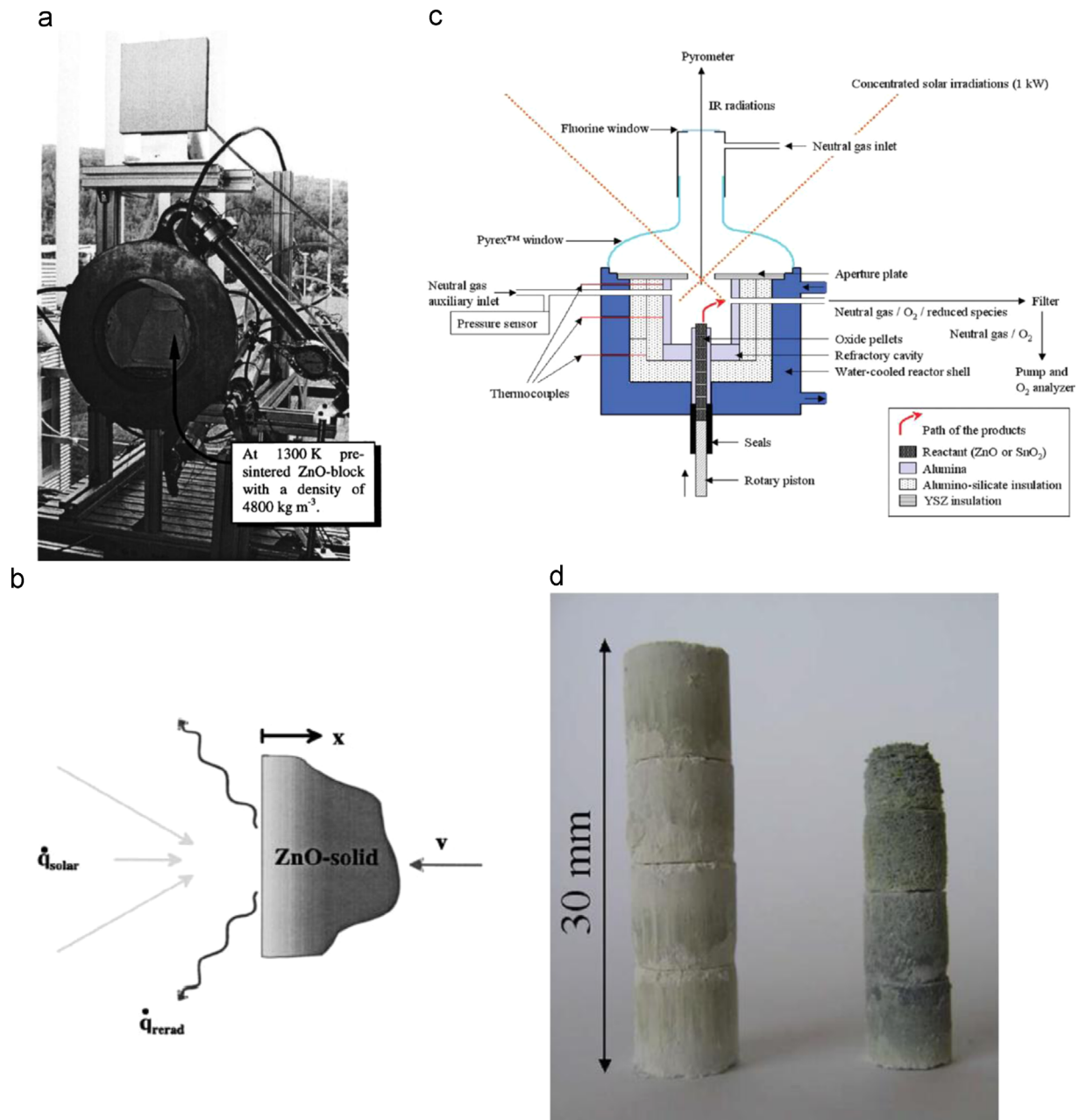


Fig. 5. Moving front solar reactors for the solar thermal dissociation of ZnO (or SnO_2): (a) the solar reactor of PSI/ETH tested and (b) its irradiation principle (from [179]); (c) schematic of the experimental setup of the solar reactor of PROMES; (d) photographs of ZnO oxide pellets before (left) and after (right) high-temperature heating in PROMES's solar reactor (from [180]).

addressed by feeding the feedstock ZnO powder continuously to the (non-moving) reactor by a series of fifteen vibrating hoppers distributed along the reactor's upper perimeter (Fig. 4c). The powder thus falls as a thin sheet under gravity (aided by a minimal inert gas flow) into the reaction chamber. In there, it slides along the surface of an inverse, inclined cone consisting of Al_2O_3 tiles essentially forming a moving-bed reactive layer. The bulk reactant flow releases a small fraction ($< 5\%$ by weight) of smaller particles that are entrained as an aerosol in a stabilized vortex flow of inert gas within the reaction cavity. Being gravity-driven the reactor configuration has to be vertical and therefore heated by a beam-down solar concentration system. Modeling investigations were conducted in order to refine the design process. Experiments at the solar simulator facilities of PSI were also performed but so far only up to 1173 K to test the mechanical and structural stability and the reaction-surface adhesion process.

5.1.1.3. The moving front reactor. Problems inherently related to cavity rotation are sealing of rotating components, and facile reaction monitoring through the insertion of thermocouples/measuring probes. To circumvent such problems, both the ETH/PSI and PROMES groups have at some point attempted to substitute the redox oxide powder with shaped objects made of it, or, in other words, switch the reactor from a non-structured to a structured one.

The ETH/PSI reactor described above was modified to include ZnO blocks pre-sintered at 1300 K as solid samples positioned in the reactor at an angle of 45° with respect to the quartz window (Fig. 5a) [179]. The operation principle is depicted in Fig. 5b; essentially the solid piece is subjected to thermal ablation. Therefore if the solid specimen is not moving, firstly the front surface vaporizes and the ZnO front surface actually moves toward the back of the reactor. In the other hand, a pressed cylinder of ZnO could be continuously advanced to the focal point from the back of the reactor.

This is exactly the principle that the research group of PROMES has adopted in a recent study where they proposed, built and tested a “moving front” reactor suitable for both the SnO_2/SnO and ZnO/Zn cycles [180]. The reactor (Fig. 5c) is a vertical ceramic cavity containing the reactant solid oxide(s) into 3–8 mm-thick shaped pellets (8 mm-diameter) brought forth by compressing up to 2 g of commercial oxide powder (SnO_2 or ZnO) that were stacked in a 60 mm-long alumina feeding tube. This pile of pellets, forming an oxide “rod” (Fig. 5d) could be pushed upward via a screw piston manually rotated for achieving a continuous reactant injection during an experimental run. Therefore the reaction front is moving to be always at the focal point of the concentrated solar beams. ZnO and SnO_2 thermal dissociations were successfully performed at about 1900 K. The reactor, operating continuously, sustained repeated solar tests without significant cavity material degradations for an equilibrium temperature of about 1900 K. Each test produced about 1 g of powder with significant fractions of reduced species in less than 30 min for a pressure of 20 kPa. In addition, the mass fractions of reduced species in the synthesized SnO powders (maximum 72%) were always higher compared to Zn in similar conditions corroborating that the recombination reaction is less favored in the case of SnO. However, as the authors state “...the quenching device must be optimized in a future design via turbulent injection of neutral gas at the reactor output to improve both the yield of particle recovery and the mole fraction of reduced species in the produced powder...”.

5.1.2. Indirectly-irradiated receiver-reactors

5.1.2.1. Indirectly-irradiated aerosol reactors. Such reactors – i.e. reactors where the solid reactant is in the form of very fine

particles suspended in a gaseous stream – have been proposed and employed from the research group of University of Colorado, Boulder, U.S.A. for the ZnO dissociation reaction [181]. The idea is based on their demonstrated success in producing at an industrial scale tungsten carbide powders by the Dow Chemical Company. The particular category of aerosol reactors belongs to the so-called “hot-wall” reactors [182]. When, instead of electrically, such reactors are solar-heated, this “wall” is made of graphite which develops very high temperatures and in turn re-radiates. The idea is that fine particles in one hand can be fed continuously within rapid reaction aerosol reactors and in the other hand can be (indirectly) heated up extremely quickly due to their ability to efficiently absorb the massive radiative heat flux from the hot graphite wall eliminating the need for a cavity window. Their reactor (shown in Fig. 6a) consisted of an electrically heated graphite transport tube apparatus, segregated from the aerosol flow region by an Al_2O_3 muffle tube and being capable of attaining temperatures as high as 2123 K. The space around the element was kept free of oxygen by an Argon purge. Aerosol dissociation experiments of ZnO were performed that resulted in product particles with a variety of densities, colors, particle sizes, and oxygen content. The highest conversions to Zn were obtained for moderate temperatures (1900–1973 K) and the longest residence times (~ 1.8 s). The net conversions obtained in this study (6–17%) were claimed to be the highest yet reported in the literature for pure thermal dissociation of ZnO, suggesting that the aerosol approach could have recombination related advantages compared to other reactor configurations.

The concept was extended to non-volatile systems as well by the ETH/PSI group in particular for the reduction of ceria particles, which were flowing downwards in an Al_2O_3 cylinder in the range 1273–1873 K, counter to an Ar sweep gas flow. No solar irradiation was employed however; the reactor was electrically heated. The reduction of CeO_2 particles was demonstrated and the maximum value of δ calculated from the measurements of the total amounts of evolved oxygen was found 0.046 [183].

5.1.2.2. Indirectly-irradiated structured reactors. The concept of indirect heating for the ZnO decomposition reaction was tested further from the group of University of Colorado in cooperation with the ETH/PSI one in batch-mode experiments with pre-sintered ZnO plates instead of powders placed inside the absorber tube (Fig. 6b) [184]. The products Zn(g) and O_2 were carried by an Ar flow of 1 l/min to a quench unit incorporated at the reactor exit. The heating rate was relatively slow, about 40 K/min to avoid thermal shock, in contrast to direct-absorption reactor concepts, where the reactants are directly exposed to high-flux solar irradiation and can be heated at rates exceeding 1000 K/s [175]. No reaction was observed at below 1750 K. The average reaction rate was determined using the weight loss by the ZnO plate obtained from six experimental runs carried out in the range 1780–1975 K.

5.2. Solar reactors performing both cycle steps

The majority of such reactors are Directly-Irradiated Receiver-Reactors (DIRRs) with only one design so far being Indirectly-Irradiated one. They employ either powders or structured shapes. Different concepts are implemented to perform both steps of the cycle in a single reactor configuration; one fundamental distinction has to do with whether such reactors employ moving or only stationary parts.

Reactor concepts and designs have implemented different technical solutions in order to meet the technical requirements of the thermochemical cycle made up of two process steps

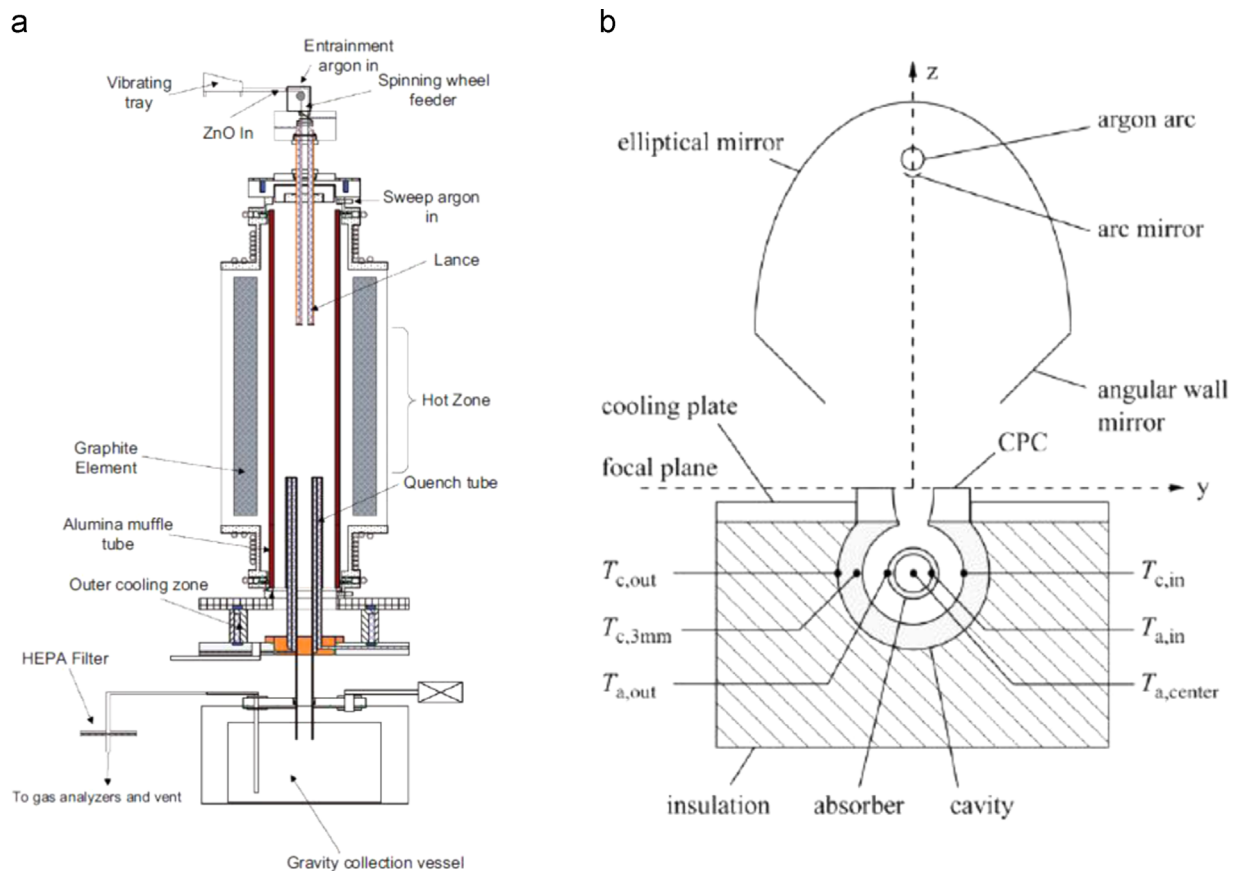


Fig. 6. IRRs proposed by the University of Colorado for ZnO dissociation: (a) schematic of the operation concept of the aerosol reactor (from [181]); (b) schematic of the solar cavity reactor where the solid material is employed in the form of pre-sintered ZnO plates (from [184]).

performed at different temperature levels with different heat demands. Two concepts exist to alternate the operating status of the reactants periodically, attaining either a continuous or a batch-wise H_2/CO /syngas production. For the former of the two reactor concepts, such continuous production is achieved by moving the reactive particles or structures from a thermal reduction reactor or zone to a splitting reactor/zone. The two reactors/zones are operated at different temperatures; at least the thermal reduction reactor is heated by solar irradiation. Gas streams and solar irradiation can be provided continuously to the reaction chambers. The second concept foresees splitting and reduction taking place in one single reaction chamber avoiding thus any solids transportation. By that means, batch-wise production of H_2/CO /syngas is achieved by switching the gas streams in the reaction chamber from reducing to oxidizing atmosphere. Simultaneously, solar flux densities need to be adjusted in order to realize the two different temperature levels and heat demands of reduction and splitting. This is typically realized by diverting the solar flux periodically. All these concepts will be presented below.

5.2.1. Non-structured directly-irradiated receiver-reactors

5.2.1.1. The packed bed reactor. A first such reactor was tested at the solar furnace of PSI [44]. It was a packed bed reactor consisting of a small quartz tube (2 cm diameter), placed in the focus of the solar furnace with a secondary concentrator behind it to provide a uniform irradiation of the tube (Fig. 7a). $Ni_{0.5}Mn_{0.5}Fe_2O_4$ powder mixed with Al_2O_3 grains was used as reactive particle bed (Fig. 7b). During TR Ar was passed through the packed bed and afterwards a mixture of Ar and steam was introduced. H_2 and O_2 evolution was observed (Fig. 7c). Even though this is the first reported solar-

aided production of hydrogen from ferrites with TR temperatures below their melting point, this concept was not followed up.

5.2.1.2. The spouted bed reactor. The research group of Niigata University, Japan, has set forth the concept of an internally circulating “fluidized” bed reactor (or, in a more precise terminology, a “spouted” bed reactor) to be combined with a beam-down solar concentrating system, in a series of publications [87,88,185–187]. A schematic of the operating concept and a photograph of such a reactor operating while irradiated by a solar simulator are shown in Fig. 8a. The redox oxide particles are circulated through an internal annulus from the bottom to the top of the reactor and are exposed to concentrated solar radiation entering from a window at the top, at the uppermost points of their trajectories. The idea is that internal circulation will, among others, inhibit sintering and agglomeration of the redox oxide particles avoiding hence a pulverization process after the TR step. In addition, sequential performance of the two steps of the cycle would be possible in a single reactor by switching the feed gas between an inert gas (N_2) for the TR step to steam/ CO_2 for the WS/CDS step. On the basis of this concept, such chemical reactors were tested for TR with unsupported $NiFe_2O_4$ as well as supported $NiFe_2O_4/ZrO_2$ particles on a laboratory scale using solar-simulating Xe-beam direct irradiation. First tests involved only the TR reaction, removing the reduced powder and performing in another non-solar rig the WS reaction, whereas subsequently both steps were tested in the same spouted bed reactor [88]. During these tests the temperature at the surface of the fluidized particle bed during TR step reached 1773–1873 K in the draft tube region and 1373–1523 K in the annulus region. Approximately 35%

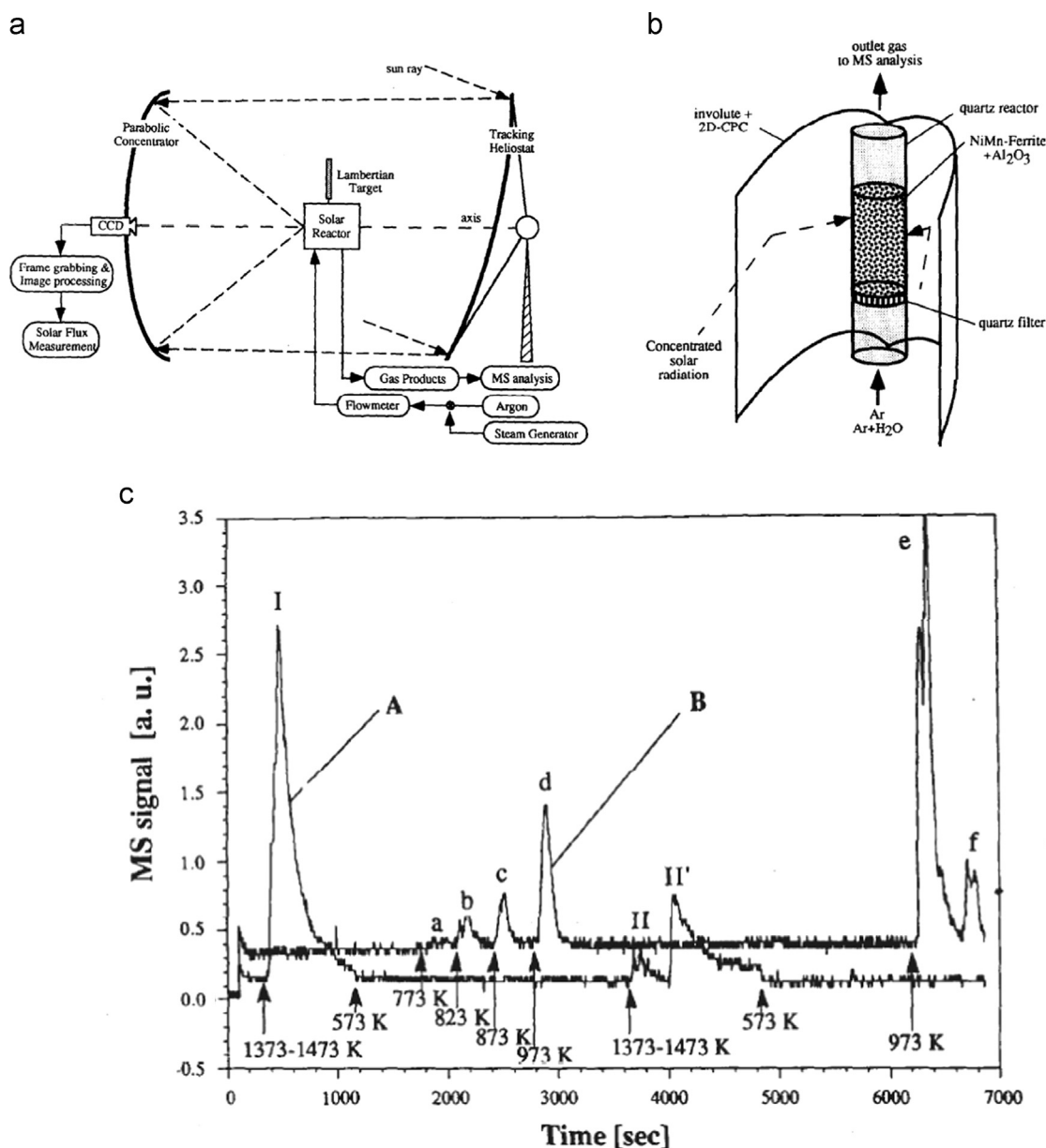


Fig. 7. Solar hydrogen production via ferrites at PSI, Switzerland: (a) sketch of the experimental set-up in the solar furnace; (b) schematic of the solar receiver-reactor packed bed configuration; (c) oxygen (curve A) and hydrogen (curve B) signals, monitored by MS, during CSP-aided thermal reduction and water-splitting reactions (from [44]).

of the supported NiFe_2O_4 was reported to have been converted to the reduced phase, and subsequently completely re-oxidized with steam at 1373 K to generate H_2 , remaining in powder form without sintering and agglomerating during Xe-beam irradiation over 30 min.

5.2.1.3. The moving packed bed reactor. Recently, another reactor concept, based on a continuously moving packed bed of redox oxide particles, was proposed by a consortium of U.S. researchers from SNL, Bucknell University and Arizona State University [188]. A schematic of its operating principle is shown in Fig. 8b. The oxide particles in their oxidized state are transported by a vertical screw elevator/feeder with a rotating casing to the top of a solar tower, where concentrated solar radiation enters through a window-covered aperture, directly heating and thermally reducing them. This step produces gas phase O_2 , which is pumped away from the chamber. The central idea is that of effective heat recuperation

since the packed bed of the reduced particles produced, is then supposed to move downwards via a connecting tube in a counter-flow arrangement with respect to the oxidized particles moving upwards, essentially pre-heating them. Heat transfer via conduction, from the hot (reduced) particles to the colder (oxidized) ones is augmented by the extended surface area of the conveyor auger. In this respect the whole reactor consists of three sections: a thermal reduction chamber at the top, a recuperator (solid–solid heat exchanger) in the middle and a fuel production chamber (at the bottom). In the fuel production chamber, the particles are exposed to reactant gases (H_2O or CO_2) reducing them to fuel products (H_2 or CO). The mix of reactants and products ($\text{H}_2\text{O}/\text{H}_2$ or CO_2/CO) is removed from the chamber and the reoxidized particles are fed into a return elevator that brings them to the inlet of the recuperator/elevator to continue the cyclic process. Advantages claimed are spatial separation of pressures, temperature and reaction products in the reactor; solid–solid sensible heat recovery between reaction

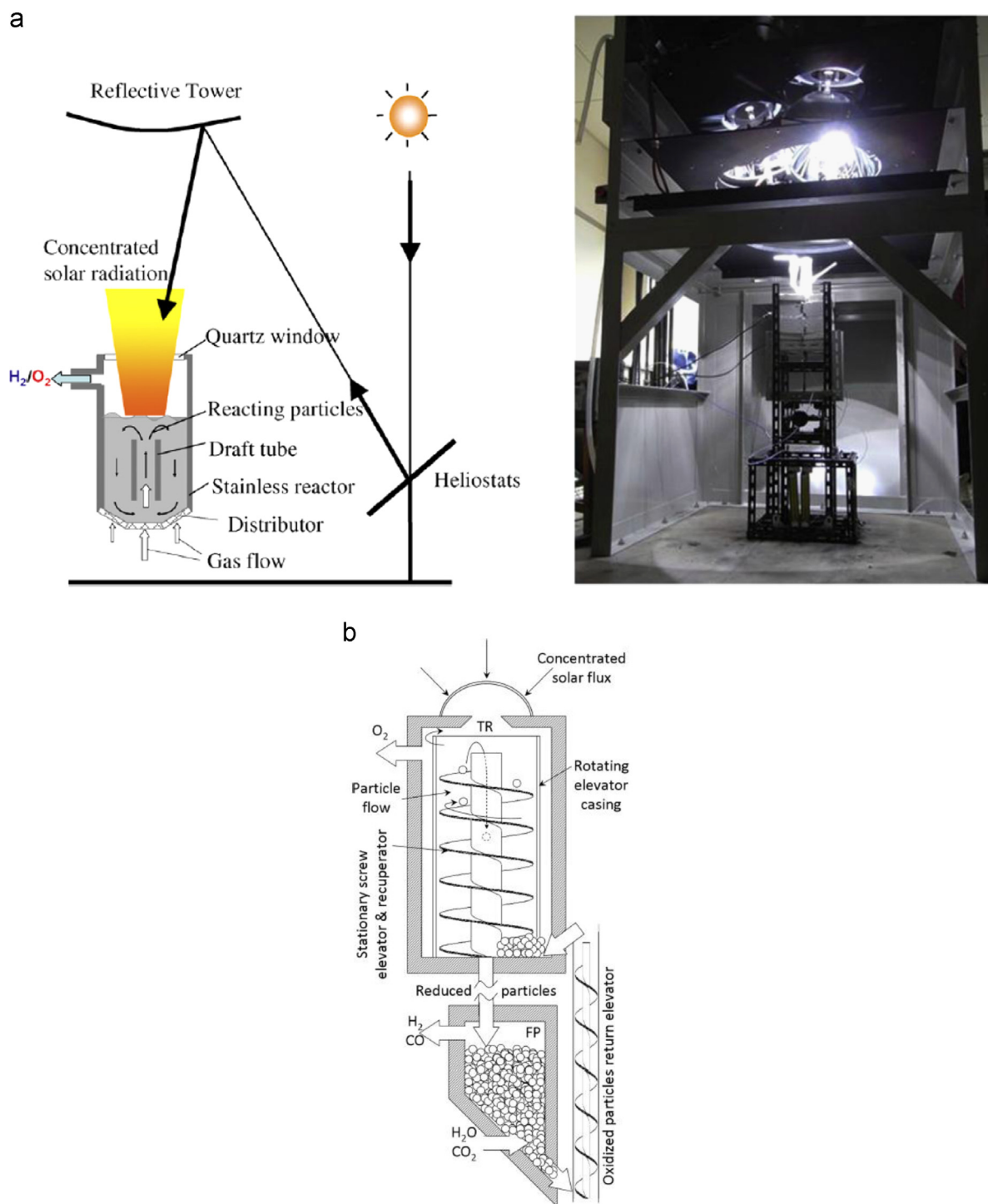


Fig. 8. Solar reactors employing moving powder beds: (a) the spouted bed reactor of Niigata University, Japan: schematic of the operation concept and actual photograph of such a reactor operating while irradiated by a solar simulator (from [88]); (b) operating principle schematic of the moving packed bed redox solar reactor proposed by Sandia Labs., Bucknell University and Arizona State University (from [188]).

steps; continuous on-sun operation and direct solar illumination of the working material. It is also claimed that vacuum pumping of the thermal reduction half of the cycle – i.e. operating the entire reactor at sub-ambient pressure – made possible by pressure separation in the particular reactor design, has a decisive efficiency advantage over inert gas sweeping currently explored. Conversion efficiencies of solar energy into H_2 and CO exceeding 30% have been reported by simulations, using CeO_2 as a reactive material. However this concept has not been experimentally implemented and tested as yet.

5.2.2. Structured directly-irradiated receiver–reactors with non-moving parts

As already mentioned, such reactors stem from the traditional gas–solid catalytic chemical reactors, where ceramic porous supports, chemically inert with respect to the targeted reactions, are coated with a catalyst material capable to catalyse them. The evolution of such solar receiver–reactors proceeded along this developmental path for some time, i.e. by depositing layers of redox oxide materials upon ceramic supports capable of absorbing the concentrated solar irradiation and developing the temperatures

required for the TR step. As more and more experience was accumulated with such systems, it was at some point realized that in one hand possible side reactions of the redox coating with the support material could have an adverse effect on the desired reactions and that in the other hand the much larger thermal mass of the redox-inert support material had an adverse effect on the reactor's thermal efficiency. In this perspective a self-supported, shaped, porous structure – e.g. honeycomb, foam or fin – incorporating the maximum possible amount of a redox oxide in its structure instead of a thin coating layer (and even better, entirely made out of it) would introduce minimal thermal mass that is not directly involved with the reaction process into the reactor and consequently higher volumetric product yields and enhanced efficiency. Therefore, recent efforts have been shifted in this direction; the relevant developments are presented below.

5.2.2.1. Reactors based on ceramic honeycombs. The first examples of honeycomb reactors for solar-aided chemistry applications can be traced back to 1989. Researchers at WIS have deposited Rh first on alumina and then on cordierite honeycombs and irradiated it in their solar furnace to catalyze the reaction of CO₂ methane reforming [189,190]. However such honeycomb reactors have not been scaled-up until 2006, when the HYDROSOL research group (including among others the research group of APTL, Greece and the present authors) has introduced the concept of monolithic, honeycomb solar reactors for performing redox pair cycles for the production of hydrogen from the splitting of steam using solar energy [191]. The reactor, was inspired in one hand from solar-radiation-absorbing honeycomb volumetric receivers made of silicon carbide (SiC) employed in air-operated solar tower power plants [173,192,193] and in the other hand from the well-known automobile catalytic converters [194]. The concept is based on the incorporation of active redox pair powders as coatings on multi-channeled monolithic honeycomb structures capable of achieving and sustaining high temperatures when irradiated with concentrated solar irradiation. The operating sequence is shown in Fig. 9a: when steam passes through the solar reactor, the coating material splits water vapor by “trapping” its oxygen and leaving in the effluent gas stream pure hydrogen. In a subsequent step the oxygen–“trapping” coating is thermally reduced by increasing the amount of solar heat absorbed by the reactor. Such redox-material-coated-honeycombs (Fig. 9b) have achieved continuous solar-operated WS–TR cycles. The issue of continuous production has been resolved with a modular dual-chamber fixed honeycomb absorber design and implementation shown in Fig. 9c [195]. One part of modules splits water while the other is being regenerated; after completion of the reactions, the regenerated modules are switched to the splitting process and vice versa by switching the feed gas [196]. Due to its modularity and the lack of moving parts, this design is amenable to straightforward scale-up and can be effectively coupled with a solar platform facility placed on a solar tower for continuous mass production of hydrogen. Indeed, such a modular, dual-chamber, ferrite-coated-honeycomb HYDROSOL reactor has been scaled up to the 100 kW level, coupled on a solar tower facility (Plataforma Solar de Almería, Spain) and achieved continuous solar-operated WS–TR cycles demonstrating the “proof-of-concept” of the proposed design (Fig. 9d and e) [197]. In such a facility, the different heat demands for the two process stages were realized not by moving the reactors, but by adjusting the flux density on each module when the status of the cycle is switched from regeneration to splitting and vice versa. This was achieved via partitioning the heliostat field and providing two “switchable” focal spots with independent power modulation [198].

An optimization of the reactor shape has been carried out to reduce the quite high re-radiation losses due to the high temperatures and the large exposed absorber surface area revealed by experiments and simulations [199]. A new reactor design has been proposed [200] where the overall shape of the absorber is close to a hemisphere and a suitable secondary reflector is included as well (Fig. 9f and g). The reactor–receiver consists of two parts: a receiver “flat” part made of non-redox, square-shaped honeycombs at the front plate of the reactor (just behind the quartz window) and a “domed” part at the rear which is the reactor part consisting of the redox-coated modules. These are of three different shapes, pentagonal, hexagonal and half-hexagonal for realizing an almost spherical structure, the so-called “football shape” (a truncated icosahedron, of the family of Archimedean bodies). The introduction of a spherical shape of the absorber and a suitable secondary reflector ensures a more homogeneously distributed solar flux and therefore a more homogeneous temperature distribution than that of the previous, “flat design” version. The cavity design ensures also that the thermal radiation is rather absorbed inside the reactor than emitted through the window since different parts of the absorber face each other instead of facing the environment like in the previous flat design. Furthermore, the whole reactor set-up and all components were designed in a way allowing easy maintenance and replacement of parts, in particular of the individual absorber monoliths.

The approach of directly fabricating the redox powders into monolithic, honeycomb-type structures was adopted from the SNL group even though designed to be integrated into another reactor design concept (to be discussed below). They employed robocasting for free-form processing of ceramics to manufacture monolithic structures [90]. Physical mixtures of ferrite powder with various supports were fabricated directly into small-scale, three-dimensional lattice structured monoliths with dense and porous rods after firing at 1700 K with design objectives of high geometric surface area, thermal shock resistance and allowance for light penetration. Photographs of such items are shown in Fig. 10a [201]. Such cast objects made of 1:3 Co_{0.67}Fe_{2.33}O₄/YSZ, Co_{0.67}Fe_{2.33}O₄/Al₂O₃ and Co_{0.67}Fe_{2.33}O₄/TiO₂ were tested for cyclic TR/WS in a typical, laboratory-scale, non-solar-heated flow reactor between approximately 1673 K (TR) and 1273 K (WS). Structural integrity could be maintained over successive cycles, however only the first composition was proved capable of cyclic WS/TR operation. The authors attributed this to probable reaction of the ferrite with the support to iron spinels (e.g. FeAl₂O₄ and Fe₂TiO₄) in the other two cases. The work was continued along the same approach with (CeO₂)_{0.25}(ZrO₂)_{0.75} monoliths cast in a similar fashion, which were shown capable of WS as well as CDS and in fact exhibiting greater yield of CO relative to H₂.

Exploring the same issue of maximum incorporation of redox oxide in the receiver–reactor's structure, a U.S.A. research consortium from SNL, University of Arizona and Missouri University of Science and Technology, proceeded in the co-extrusion of zirconia–iron oxide honeycomb substrates to be tested for solar-based thermochemical CDS [202]. The test material was formed from 75 vol% YSZ and 25 vol% Fe₂O₃ processed into honeycombs of cell sizes 2.4, 4.0, or 6.0 mm in diameter, by the polymer-based co-extrusion of ceramics (Fig. 10b). The chemistry and oxygen transport properties of the support phase were altered by using zirconia with either 3 or 8 mol% yttria additions, producing a low conductivity–(YSZ-3) and a high conductivity-support phase (YSZ-8). The extruded specimens were sintered at 1673 K before finally tested in a laboratory scale test furnace for CDS. The TR step was performed at 1743 K under He and the CDS step at temperatures of 1173 K, 1273 K, 1373 K and 1473 K. It was reported that the melting of FeO at high temperature allows for full reduction of the substrate system in a very short time period (< 60 min), making

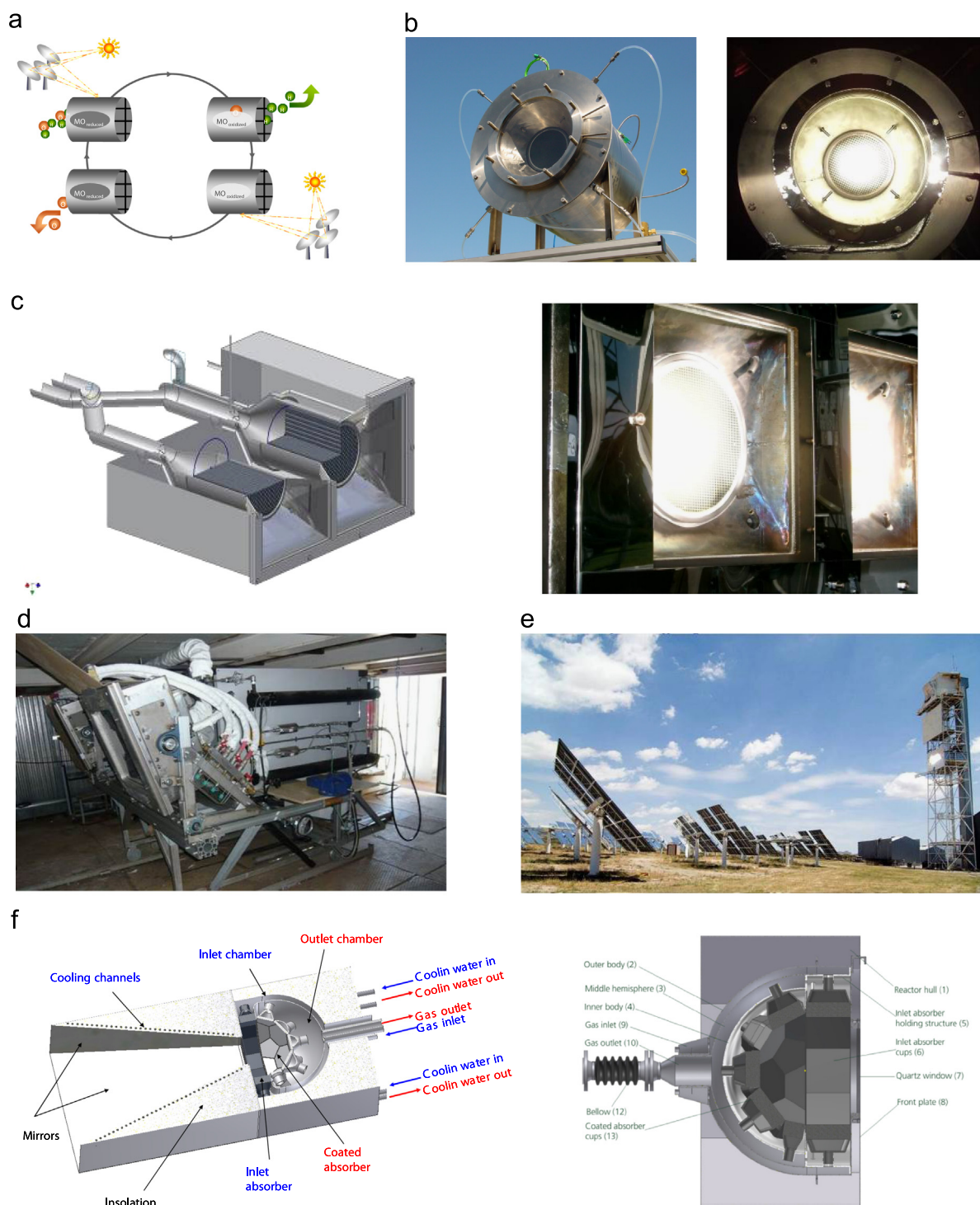


Fig. 9. Solar reactors employing honeycombs; the HYDROSOL reactor technology evolution: (a) operating concept; (b) first single-chamber reactor assembled and in operation (from [191]); (c) the continuous solar hydrogen production operation concept and the first dual-chamber reactor in operation (from [195]); (d) the 100 kW_{th}-scale dual-chamber reactor on the top of the PSA solar tower (from [197]); (e) operation of the reactor coupled with the solar field; (f) schematic illustration of the 100 MW complete reactor module with secondary concentrator and of the absorber/reactor module design (from [200]).

it highly reactive for CO₂ generation cycles. The honeycomb substrates survived 6–10 cycles of melting at high temperature without significant deformation or structural failure (Fig. 10c).

5.2.2.2. Reactors based on ceramic foams. Such reactors based on ceramic foams were the first structured reactors tested in solar chemistry applications—in fact for solar-aided syngas production via CO₂ (dry) methane reforming in a 100 kW directly irradiated

volumetric receiver–reactor mounted on a solar thermal concentrating dish, by SNL and DLR [203] between 1987 and 1990. Although the above concept has been progressively scaled-up to the 400 kW_e level [204–206] such foam-based reactors were not used until recently for solar-aided “splitting” reactions (either WS or CDS). The first study on ceramic foams coated with redox materials for WS is reported by the group of Niigata University, Japan [207]. Therein a ceramic foam made of Magnesia-Partially-Stabilized Zirconia (MPSZ) was coated with Fe₃O₄ and c-YSZ

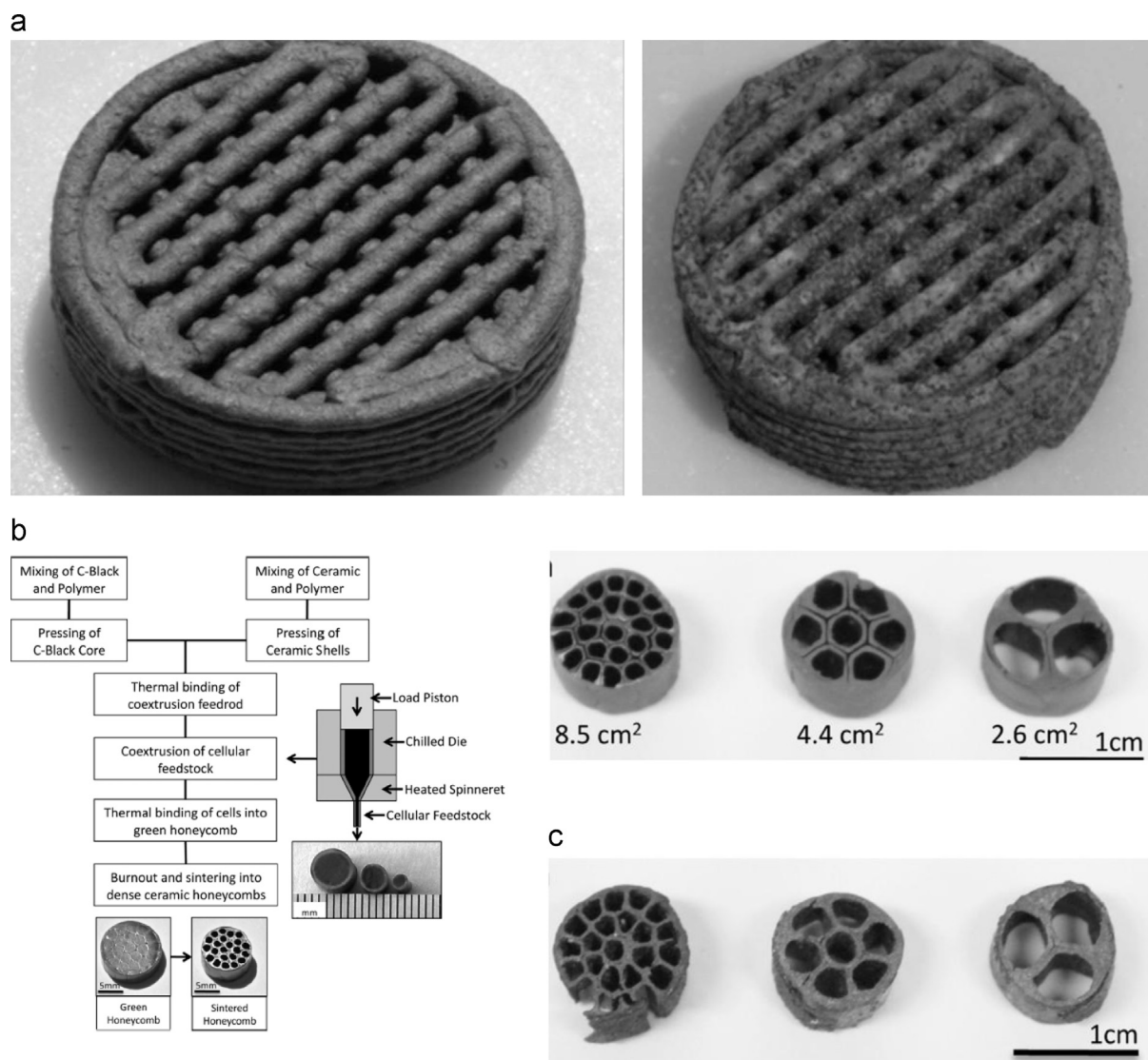


Fig. 10. Solar reactors employing honeycombs; SNL-produced honeycomb structures used for solar-aided WS/CDS: (a) robo-cast cobalt ferrite/zirconia cylindrical pellets ($\approx 15 \text{ mm } \varnothing \times 5.4 \text{ mm}$ thick) tested for cyclic TR/WS, as-cast and after 31 thermal reduction and water oxidation cycles (from [90]). Coextruded YSZ- Fe_2O_3 honeycombs of SNL's consortium: (b) schematics flow diagram for the processing of polymer-based co-extrusion ceramic honeycombs; (c) photographs of the coextruded honeycomb substrates prior to (top) and after (bottom) thermochemical CDS testing (from [202]).

particles and examined as a thermochemical WS device. The two cycle steps were performed in independent reactor rigs: WS under irradiation of a Xe lamp at 1073 K (Fig. 11a) and TR in an electrically-heated tube furnace at 1373 K (Fig. 11b) with Fe_3O_4 loading amounts of 4.0 wt%, 6.9 wt% and 10.5 wt%. Throughout 32 cycles of the two-step WS reaction, H_2 production was successfully continued; however at that point the YSZ/MPSZ foam device was cracked and broken (Fig. 11c). The work was continued with m-ZrO₂-supported NiFe_2O_4 and Fe_3O_4 powders [208]. Eventually the most reactive foam device of $\text{NiFe}_2\text{O}_4/\text{m-ZrO}_2/\text{MPSZ}$ was tested in a windowed single reactor using solar-simulated Xe-beam irradiation with a power input of 0.4–0.7 kW_{th}, producing successfully hydrogen for 20 cycles [209]. The group is conducting a solar demonstration project of thermochemical WS at Inha University in Korea using a larger $\text{NiFe}_2\text{O}_4/\text{m-ZrO}_2$ -coated MPSZ foam device with a 5-kW_{th} dish concentrator (Fig. 11d).

The ETH/PSI group in collaboration with the group of Caltech developed a solar reactor based on reticulated porous ceramic foams manufactured entirely from the redox material – cerium oxide (CeO_2) in the particular case – for thermochemical CDS. Actually this has occurred as a culmination of their work

employing initially pellets, then porous cylinders, fibers and eventually foams made entirely of the particular redox material. The evolution of their technology of ceria-based solar cavity reactors for solar-driven thermochemical production of fuels is depicted in Fig. 12. In their first such experiments they employed CeO_2 and $\text{Sm}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ annealed for 3 h at 1773 K to perform separately WS and CDS [40]. In the former case, the materials were shaped in the form of 65% porous pellets loaded into a tubular reactor inside an IR furnace and operated for 400 cycles. With respect to the TR step, upon heating to 1773 K under an inert atmosphere ($p_{\text{O}_2} = 10^{-5} \text{ atm}$) release of oxygen was observed whereas ceria reduction at 1873 K resulted in higher oxygen yield. Hydrogen production was observed by introducing steam at 1073 K with the total amount of hydrogen produced implying complete re-oxidation of the reduced ceria. The first solar campaign was reported by the same group [36] employing a cavity receiver containing a porous monolithic ceria cylinder directly exposed to concentrated solar radiation impinging on its inner walls for the (separate) two-step, solar-driven thermochemical WS and CDS (Fig. 12a). TR of ceria was performed at $\approx 1873 \text{ K}$ and CDS at $\approx 1173 \text{ K}$. An analogous set of experiments was performed for

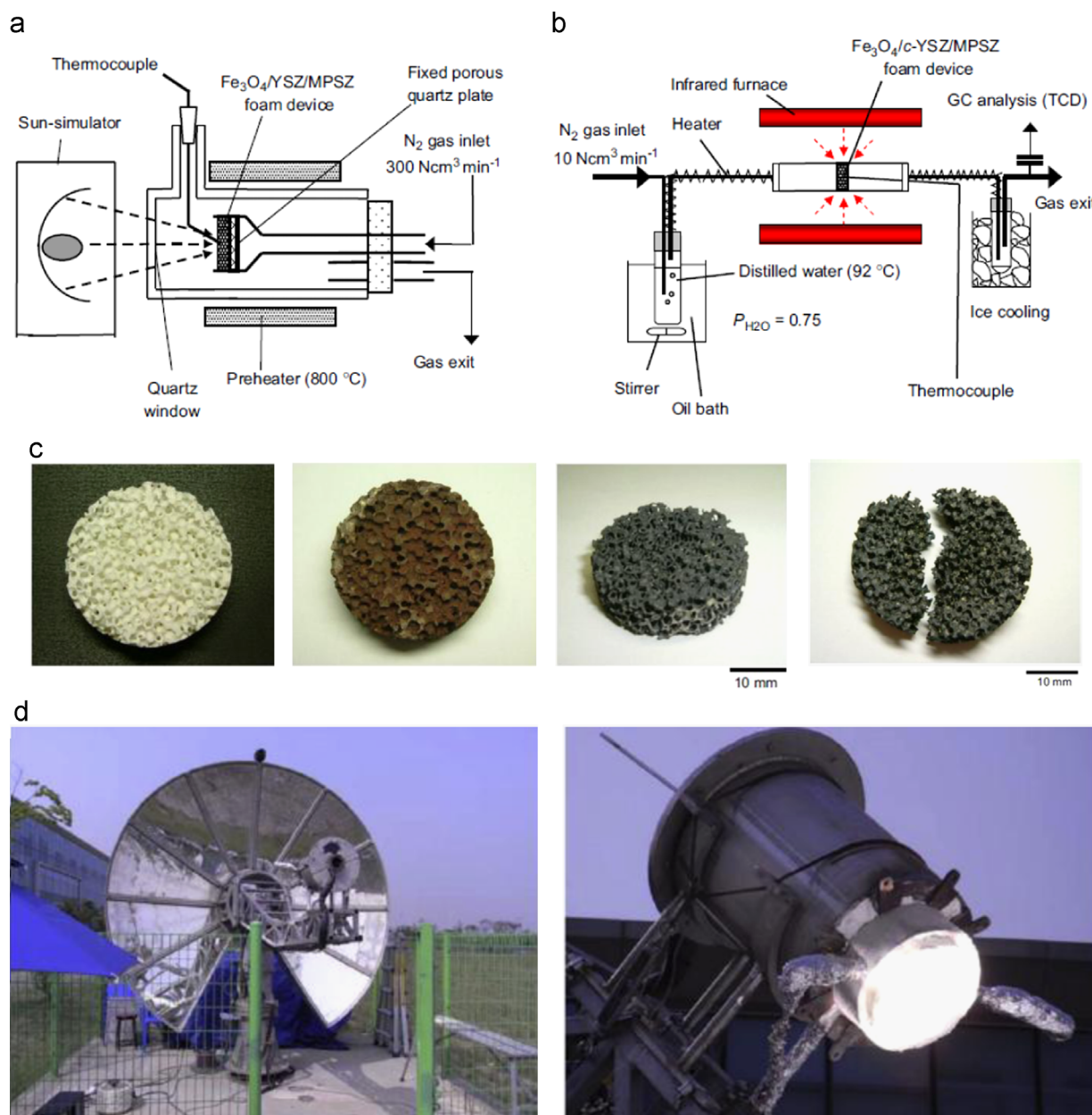


Fig. 11. Solar reactors employing ceramic foams; experimental apparatus of Niigata University for (a) the TR step and (b) the WD step using the $\text{Fe}_3\text{O}_4/\text{YSZ}/\text{MPSZ}$ foam device; (c) from left to right: photographs of the non-coated MgO partially stabilized zirconia (MPSZ) foam, the $\text{Fe}_3\text{O}_4/\text{YSZ}$ coated MPSZ foam before testing, the same foam after 11 cycles and the same foam after 32 cycles when cracked (from [207]); (d) photographs of the 5-kW_{th} Inha University's dish concentrator in Korea: left photograph; front side of dish concentrator; right photograph: solar foam reactor installed (from [209]).

H_2O dissociation for 500 WS cycles, where the most obvious feature was the much faster rate of fuel production than that of O_2 release. In a subsequent work [210] they employed a solar cavity-receiver containing porous ceria felt directly exposed to concentrated thermal radiation provided by a solar simulator. TR of ceria was performed at 1800 K and re-oxidation with a gas mixture of H_2O and CO_2 at 1100 K, producing syngas with H_2/CO molar ratios from 0.25 to 2.34. Even though CeO_2 sublimation was observed, ten consecutive $\text{H}_2\text{O}/\text{CO}_2$ splitting cycles have been performed. Based on the above, they have recently prepared and tested in lab-scale, solar-thermal configuration (1873 K) reticulated porous ceramic foams manufactured entirely from CeO_2 (Fig. 12c) for CDS [211]. Currently, the consortium is working toward the optimization of the solar reactor (Fig. 12d) for the combination of the two thermochemical splitting cycles for solar

syngas synthesis, targeted eventually to the production of liquid aviation fuels like kerosene via post-solar FT route.

5.2.3. Structured directly-irradiated receiver-reactors with moving parts

5.2.3.1. Rotary-type reactors. In 2006, the research group from the University of Tokyo, Japan, introduced the concept of a rotary-type reactor in which a cylindrical rotor coated with redox pair materials is rotating between two chambers. In one of the chambers the WS reaction (H_2 -generation reaction cell) is performed and in the other the TR reaction (O_2 -releasing reaction cell) under solar irradiation [212]. Such a cylindrical rotor reactor of 40 mm diameter (Fig. 13a) coated separately with CeO_2 and mixed ferrites ($\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$) was fabricated

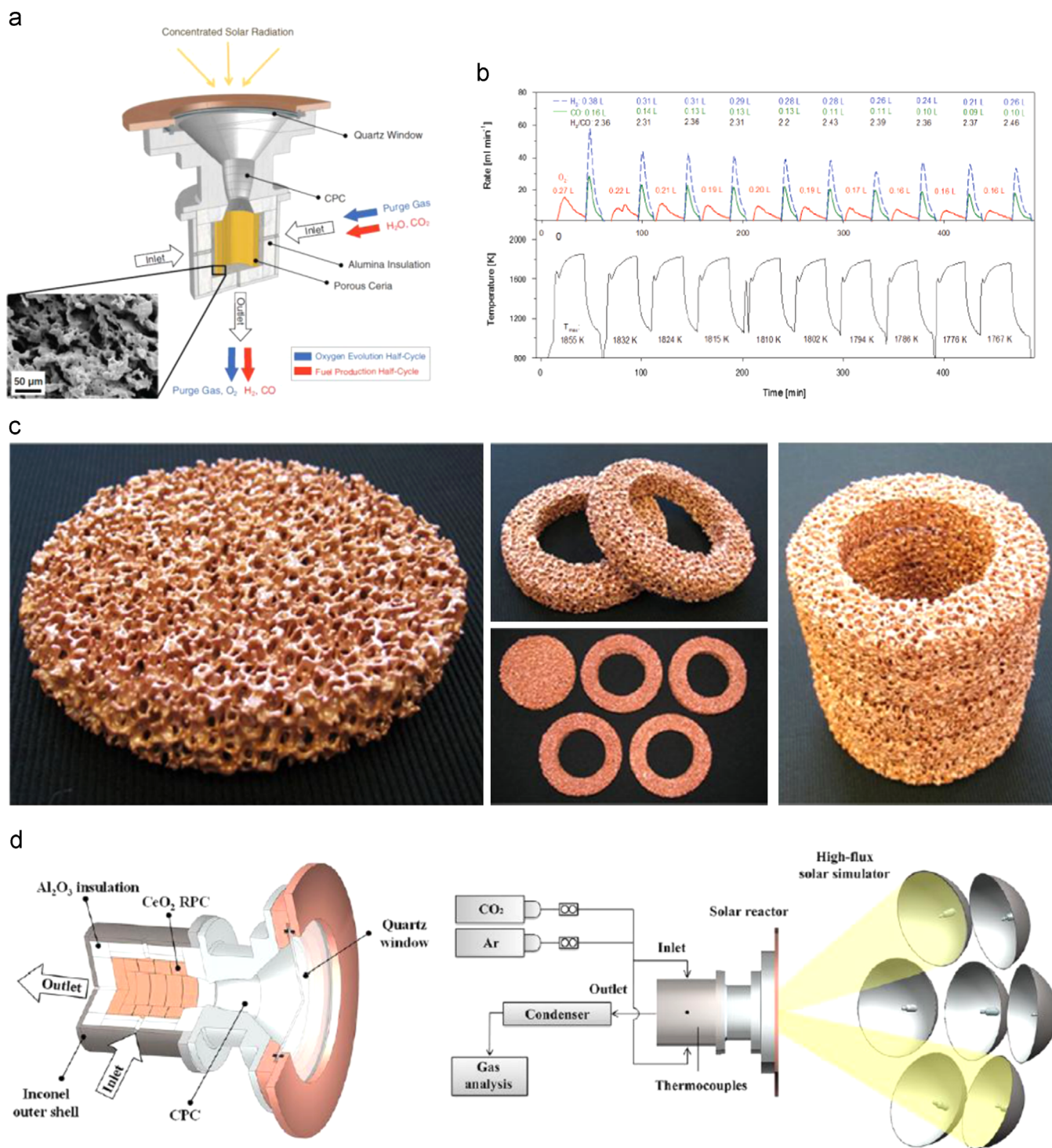


Fig. 12. Solar reactors employing ceramic foams; technology evolution of ETH's ceria-based solar cavity reactors for two-step, solar-driven thermochemical production of fuels: (a) schematic of operating principle of first solar reactor containing a porous ceria cylinder (from [36]); (b) temperature of ceria, gas production rates, total amount of evolved gases, and $H_2:CO$ molar ratios during 10 consecutive splitting cycles with a 3 kW solar reactor prototype employing ceria felt (from [210]); (c) CeO_2 reticulated parts (20 mm thickness, 100 mm o.d.) fabricated; (d) schematic of the solar reactor configuration employing ceria foams and experimental test setup at ETH's High-Flux Solar Simulator (from [211]).

and tested under IR lamp irradiation [213]. Successive evolution of H_2 gas was reported under temperatures of 1623 K in the O_2 -releasing reaction cell and 1273 K in the H_2 -generation reaction cell for CeO_2 . Also, repetition of the two-step WS process was achieved using the (Ni, Mn) ferrite with reported optimum reaction temperatures of the O_2 -releasing and H_2 -generation reactions as 1473 and 1173 K. A scaled-up version was manufactured (Fig. 13b)

with $0.8CeO_2-0.2ZrO_2$ solid solution as the selected redox material. Preliminary tests of the reactor were performed using a solar simulator of concentrated Xe lamp beams between 1473 K and 1773 K demonstrating cyclic H_2 production without sintering of the redox material [214]. This reactor was eventually tested in the solar tower facility of CSIRO, Newcastle, Australia but results of the campaign have not been published as yet.

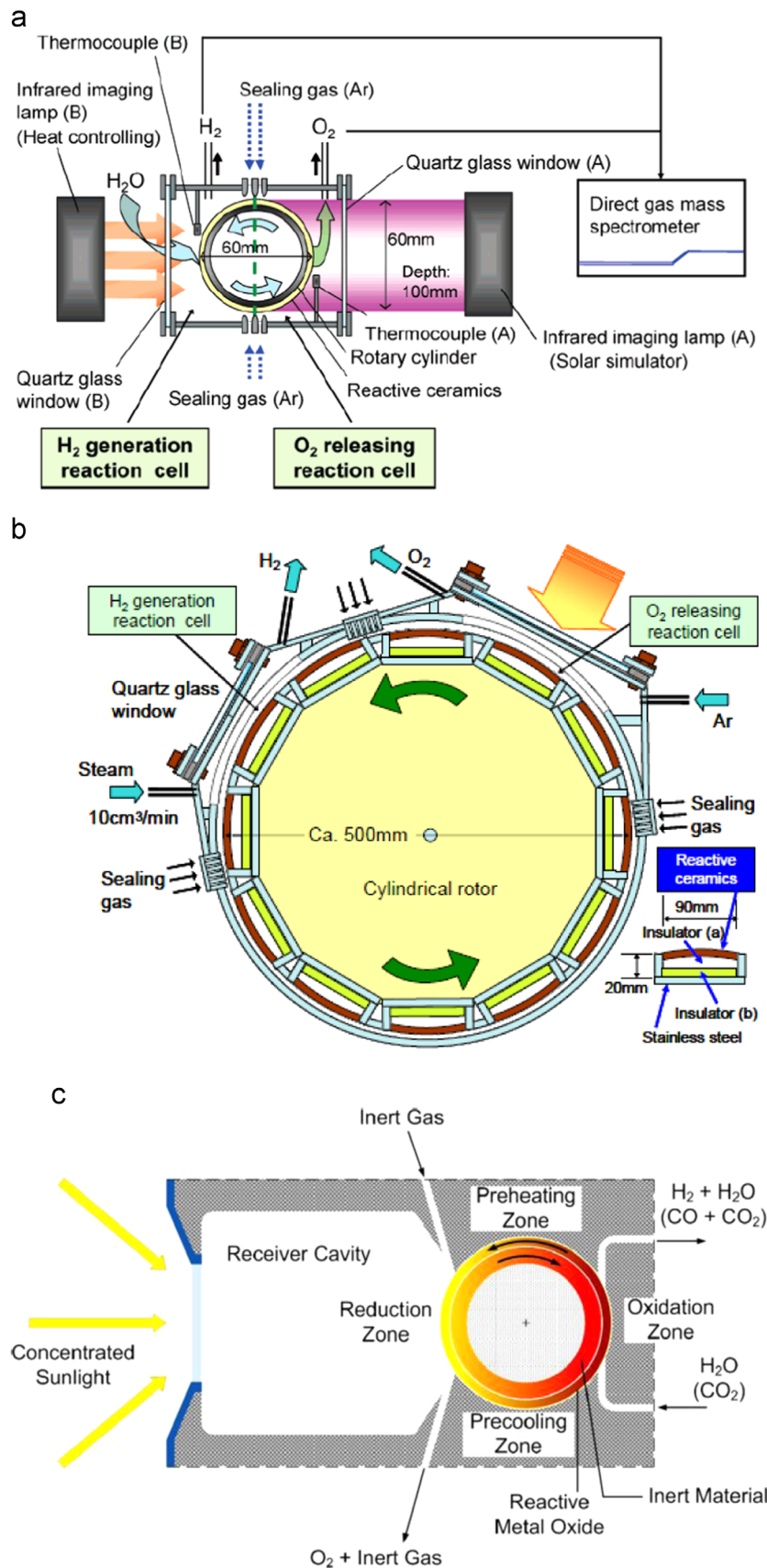


Fig. 13. Solar rotary-type reactors employing moving parts for the two-step process; (a) and (b) solar reactor of the University of Tokyo, Japan: schematic outlines of: (a) laboratory-scale version and (b) scaled-up version with 500 mm cylindrical rotor diameter (from [213]); (c) operating principle schematic of the rotating solar thermochemical reactor proposed by the University of Minnesota (from [215]).

Recently, the group of University of Minnesota has proposed another version of such a continuously operating, rotating-cylinder reactor, for production of syngas from water and carbon dioxide. The basic idea involves heat recuperation from a rotating hollow cylinder of a porous reactive material to a counter-rotating inert solid cylinder via radiative transfer (Fig. 13c) [215]. The outer cylinder consists of a reactive porous medium and cycles between the reduction zone at high temperature and oxidation zone at low temperature. The inner cylinder is a chemically inert, heat recuperating solid. Heat transfer modeling studies predicted heat

recovery effectiveness of over 50% when thin cylinder walls and long rotation periods of several minutes are employed; however no actual implementation of such a reactor has been reported yet.

5.2.3.2. *The CR5 reactor.* Also in 2006, the research group at SNL proposed their own concept of a rotating reactor, the so-called Counter-Rotating-Ring Receiver-Reactor-Recuperator (abbr. CR5) for producing hydrogen and oxygen from water [93,216]. The key feature of the CR5 is a stack of counter-rotating rings or disks that

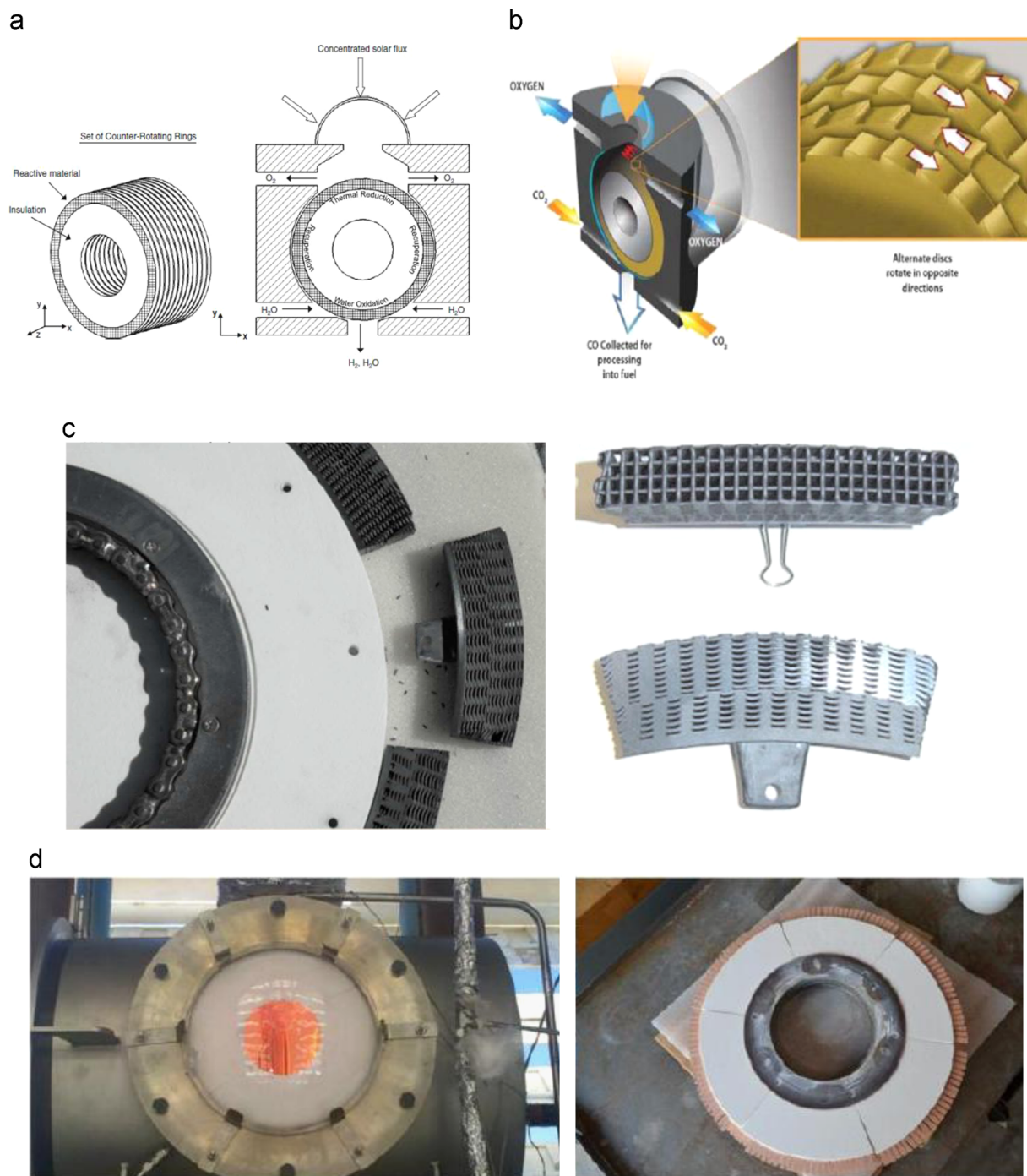


Fig. 14. Solar reactors employing moving parts for the two-step process; SANDIA's Counter-Rotating-Ring Receiver-Reactor-Recuperator (CR5): (a) schematic illustration of operating principle for water splitting (from [93]); (b) schematic illustration of operation for carbon dioxide splitting; (c) robo-cast reactant ring assembly and prototype reactant fin segments; (d) photo of the CR5 taken shortly after the conclusion of a successful 4-ring test (with ceria) and ring segments recovered after the test showing ceria fins (pink), zirconia carrier segments (white), and metallic central hub (grey) (from [219]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

are outfitted with fins around the circumference that are constructed of a redox metal oxide. The principle of its operation was conceived as follows: as the rings rotate, the reactive material passes from a solar-irradiated high-temperature TR receiver–reactor to a relatively low-temperature hydrolysis reactor where the reactant material performs a WS reaction, and then back again (Fig. 14a). That is, the fins are cyclically heated and reduced, and then cooled and oxidized. Each ring rotates in the opposite direction to its neighbor at a rotational speed on the order of one RPM or less. As the oxidized redox material in the fins leaves the WS reactor and enters the recuperator it “sees” hotter fins leaving the TR reactor on both sides. In the recuperator it heats up as the neighboring fins moving in the opposite direction cool.

SNL proposed combining the two splitting cycles (of water and carbon dioxide) with the CR5 reactor (Fig. 14b) into a project named “Sunshine to Petrol” (S2P). The project was targeted to splitting carbon dioxide into oxygen and carbon monoxide with the latter to be used afterwards for the production of hydrogen or of liquid synthetic fuels (e.g. methanol, diesel, etc.) [217]. The ultimate goal of the S2P project was that the CR5 reactor would become a building block for the synthesis of liquid combustible fuels. From an engineering design standpoint, the working redox oxide must be amenable to fabrication into physical forms that can be integrated into the engine design concept. This led the group initially to the approach of directly fabricating the reactant fin sections for the CR5 prototype by the same robo-casting technique mentioned already above [90]. Photographs of such items are shown in Fig. 14c [218]. However, the bulk of the on-sun testing effort with the CR5 reactor was performed with thin ceria fins fabricated by a casting/lamination/laser cutting methodology, captured within a zirconia-based carrier ring that is in turn captured by a metal hub (Fig. 14d). During operation, Argon is injected into the reduction side of the CR5 while CO_2 is provided to the oxidation side. In operation with 4 and 8 ceria-finned rotating rings, CDS was demonstrated successfully. In general, the CO yield increased with increasing reduction temperature and increasing CO_2 (and total) flow rate. The efficiency significantly increased when the reduction temperature was increased from 1723 K to 1823 K, but the increase was less pronounced when increasing the temperature to 1893 K. However when the scaled-up version of 22

fins was tested, operation ceased shortly, mainly since several of the rings ceased to rotate due to cracking/separation of zirconia wedge segments at or near the metal/zirconia connection points [219,220].

5.2.4. Non-structured (packed bed) indirectly-irradiated receiver-reactors

The only such reactor employed so far, was tested by the University of Colorado group for cyclic WS/CDS via the hercynite cycle [221] in a solar cavity reactor prototype, installed at the focal point of the National Renewable Energy Laboratory's (NREL) High Flux Solar Furnace (Fig. 15). The central, SiC, tube of the reactor was converted into a packed bed by placing a screen at the bottom of the tube and filling the space up to the focal point with large (1 mm) Al_2O_3 particles, Fe_2O_3 -coated via Atomic Layer Deposition (ALD), as well as with commercial Fe_2O_3 nanopowders (in separate tests) for comparison purposes. The other tubes were not filled with redox material due to its limited quantity available. Test samples were reduced under elium at 1623 K and then cooled down to 1373 K for the oxidation step during which either H_2O or CO_2 was introduced in the helium feed. Cyclic H_2 or CO productions were demonstrated with solar-to-hydrogen efficiencies of ALD particles being an order of magnitude higher compared to Fe_2O_3 powder.

6. Current development status and future prospects

The acknowledgement of the fact that the experience and technology accumulated with solar-aided, two-step, redox-pair-based WS thermochemical cycles for hydrogen production could be “transferred” to CDS and essentially culminate to the synthesis of liquid hydrocarbons from solar energy, water and (waste) carbon dioxide, has created many aspirations and research efforts worldwide. Taking into account the facts that solar energy is currently unmatched in its magnitude and availability as well as undisputedly scalable to any future energy demand this is indeed a fascinating perspective, worth exploring. However, it should not be under-estimated that despite large efforts and significant progress during the last years, hydrogen production from such solar-aided, WS thermochemical cycles, even though having been already successfully demonstrated at bench- and pilot-scale, has not yet finally solved crucial technical challenges and still has a notable way to go for potential commercial exploitation. As the present authors have already mentioned “...The reactions involved are on the edge of being feasible and practicable because high temperatures are needed and the gas–solid reactions cannot be carried out continuously (the reactive solid is consumed as the reaction proceeds)...” [171]. Technical barriers have to do both with the redox materials’ chemistry as well as the solar energy exploitation issues that were discussed above.

6.1. Redox pair materials issues

With respect to materials issues a first distinction can be made according to whether they are employed in volatile or non-volatile cycles. In volatile cycles – ZnO and SnO_2 in particular, since the other ones are currently far from being experimentally validated even in lab-scale – the volatility of Zn/SnO is not only a fundamental thermodynamic advantage but also a major technical drawback: it means that gaseous mixtures of Zn/SnO and O_2 result from ZnO/SnO_2 decomposition. Separating this mixture causes problems, since the condensation of Zn/SnO competes with their re-oxidation; i.e. essentially the same problem is encountered as with direct thermochemical splitting of water into a mixture of H_2 and O_2 gas. All such products reported so far, consist, in a lesser or

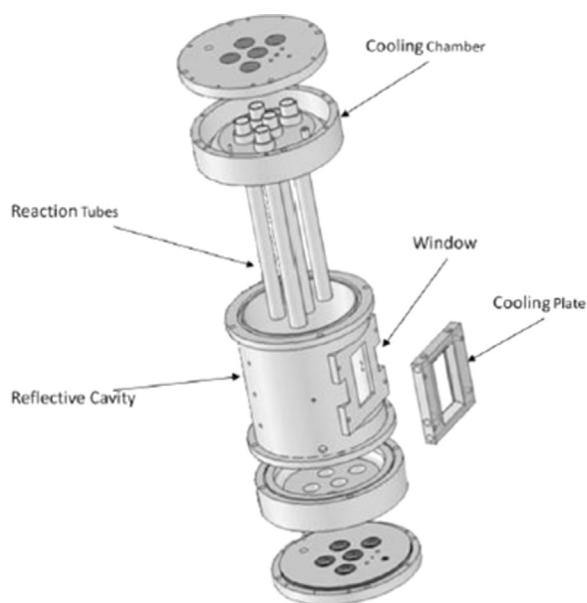
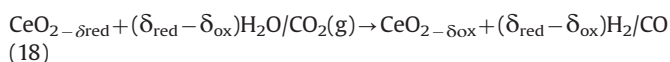
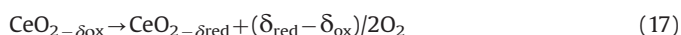


Fig. 15. Indirectly-irradiated packed bed solar cavity reactor (schematic) proposed and tested by the University of Colorado for WS/CDS via the hercynite cycle (from [221]).

higher degree, of a mixture of the reduced/oxidized state of the system. Another issue is that a complete cycle including the splitting step has not been validated yet; at the best the solar production of Zinc has been demonstrated. The common problem of all reactors to perform only the TR step is that their integration with their “oxidizing” (“splitting”) counterparts and relevant heat recuperation still needs to be demonstrated.

With respect to non-volatile cycles, materials’ screening has narrowed the selection among few material families. Nevertheless, one such family combining several desirable properties seems not to have been discovered yet. At first, even within testing such materials, many laboratory studies involved melting of the redox oxide during (solar-driven) thermal reduction, and then subsequent re-oxidation in another (not necessarily solar) reactor. Most of the times melting will be accompanied by vaporization and consequent loss of a non-negligible percentage of the redox material. Then the material has to be cooled to room temperature, grinded to fine powder and re-oxidized, making it obvious that such concepts face inherent hurdles in becoming commercially viable in large-scale.

Therefore it seems that the choices are limited within performing the cycles below the melting point of the redox pair, keeping it practically in the solid state throughout the process. Most of the materials though, operating in this mode are limited by the small width of the non-stoichiometry swing δ , discussed already in Section 2. Furthermore, the experimental results have demonstrated (the already known fact [222]) that the extension of reduction of the anyway non-stoichiometric “oxidized” state of the redox oxide in the first cycle step is not something “constant” but depends on the temperature and pressure of the experiment. This has led recently the groups active in the field [183,223] to incorporate the following nomenclature for the reaction scheme of e.g. Eqs. (11) and (12) for non-stoichiometric CeO_2 (a similar reaction scheme can be written for ferrites, perovskites etc.):



where $\text{CeO}_{2-\delta_{\text{red}}}$ represents the state of reduction reached at a particular experiment under a given temperature and pressure. The difference in the magnitude of the stoichiometric coefficients of oxygen and hydrogen/carbon monoxide between reaction pairs (7)–(8) and (17)–(18) is evident. Between the two most studied systems, ferrites and ceria, the former have demonstrated higher levels of reduction at lower temperatures. The higher TR temperatures of ceria necessitate the use of special reactor materials. In the other hand ceria is characterized by much faster gas splitting kinetics. The high oxygen yield of perovskites at moderately high temperatures perhaps can provide a future solution. Research in this direction can benefit from developments in similar, parallel paths followed for syngas production like co-electrolysis of $\text{H}_2\text{O}/\text{CO}_2$ mixtures [20] where such materials are also employed [224].

6.2. Solar reactors and heat recuperation issues

Additional concerns come into play when redox chemistry has to be coupled with solar energy. With respect to solar receiver-reactors, it is rather reasonable to expect that due to the relatively high temperatures to be encountered, directly-irradiated ones have an advantage over indirectly-irradiated. Indirectly-irradiated reactors and even allothermally-heated ones however, could become competitive if possibly combined with an open-loop system where a chemical reduction process could decrease the required temperature for the reduction step to levels close to those for instance, reachable

in future solar thermal power plants using air as a heat transfer fluid (e.g. of the order of 1173 K).

From the various worldwide research approaches involving structured reactors with non-moving parts it can be inferred that the majority of them converge in the concept of fabricating, if possible, the entire receiver-redox reactor body from the redox material itself. The concept of increasing volumetric product yield of such structured reactors by manufacturing the bulk of the entire monolithic body – that being either honeycomb or foam – from the active material rather than employing the latter as a mere coating is attractive in cases where “catalysts” for the particular reactions are relatively inexpensive materials like oxides that can be shaped to bulk finished objects (in contrast to cases where functional catalysts are e.g. expensive systems like Platinum group metals). There are arguments in favor of each structure. Honeycombs can be made with a very high density of cells per square inch (cps) to increase the mass of redox material per unit volume as well as the available gas–solid contact area. For instance, honeycomb structures for automotive exhaust aftertreatment made of oxide materials are commercially available with cell densities of 600 cps, whereas even 900 cps and 1200 cps substrates are available where wall thickness is reduced to almost 0.05 mm. For comparison, the cell density of honeycombs employed so far in solar chemistry reactors does not exceed 100 cps. Therefore a honeycomb structure made of the redox material itself and with higher cell density will have a significant impact on the enhancement of reaction rate and syngas yield. In fact such a concept has been implemented in industrial-scale. The most notable example is the manufacture of entire extruded monoliths from high-surface-area titania/vanadia and/or zeolite catalysts for the control of NO_x emissions from stationary sources (utility plants, cogeneration units, boilers’ flue gas clean up etc.) by selective catalytic reduction (SCR) with NH_3 [225]. Furthermore, the manufacture of extruded honeycombs from iron oxide (Fe_2O_3) –which is an effective catalyst for the dehydrogenation of ethylbenzene to styrene, has also been reported [226]. In the other hand foams have an inherently higher porosity that allows for solar radiation to penetrate deeper in the volume of the materials [227] complemented by a considerable degree of radial mixing. Radial mixing is a significant advantage in processes limited by heat transfer [170] and can even out flow distribution preventing flow instabilities at the high temperatures encountered during solar operation [228]. In this perspective perhaps the kind of the porous structure (honeycomb or foam) is not so crucial for solar operation but it has to be selected rather with ease-of-manufacture criteria since this modularly constructed “structured morphology” can be implemented with a variety of materials (e.g. ceria, ferrites, perovskites). A “domed” reactor like the one on Fig. 10f can be very well assembled from foam rather than from honeycomb modules like in the case of solar-aided reforming reactors [25]. It is equally obvious that the ceria foams of the reactor in Fig. 13c can be replaced with ferrite or perovskite honeycombs. Such a domed configuration complemented with a proper window can also be used for potential operation under higher pressure (just like a pressurized solar reformer). Such an operation is important because the current catalytic synthesis processes require reaction pressures of 30 bar for Fischer–Tropsch synthesis and 50 bar for methanol synthesis; thus these compression costs will be significantly reduced if any syngas synthesis route can be run above 6 bar [6].

The low efficiency of such reactors remains their main problem. The ETH/PSI group reported a peak solar-to-fuel efficiency of 3.53% at 1870 K and an average efficiency of 1.73% for the ceria-foam-based reactor. They stated that these are the highest solar-to-fuel energy conversion efficiency values reported to date for a solar-driven device converting CO_2 to CO, and more than four times

greater than previously reported values [211]; however, there is concern that perhaps such values are still over-optimistic [229]. In the other hand it is accepted among the relevant research community that the long term goal is to achieve in practical implementation, 20% solar-to-syngas energy conversion efficiency to ensure commercial viability and environmental performance as well as competition vs. alternative approaches (e.g. solar electrolysis) of solar-thermochemical fuel production [166,171,230–232]. Several of the approaches mentioned above can improve the solar fuel product yield and thus contribute toward this direction.

The implementation of efficient heat recuperation is still a major issue of concern. Many alternative solar reactor design and relevant simulations have predicted enhanced heat recuperation and reactor efficiency but when it comes to implementation, technically complicated concepts have not proved yet to have enough potential for eventual scale-up to commercially exploitable levels. For instance, to the best of the authors' knowledge, none of the proposed and tested structured reactors that include moving parts from a "hotter" region to a "colder" one to enhance such recuperation has been successfully scaled-up so far. Problems having to do with mechanical vibrations, thermal expansion, thermal shock resistance, inhomogeneous heating of rotating parts and sealing at high temperatures are difficult to overcome and become fatal during prolonged operation: such issues have caused eventual damage of reactor parts in all cases. In a similar argumentation, techniques proposing the circulation and transport of hot solid particles between higher- and lower-temperature reactor regions with the aid of mechanical parts, sometimes in combination with vacuum conditions have not been tested even at laboratory-scale yet and concepts to implement them in large-scale still need to be developed. The difficulties in scaling-up such concepts should not be overlooked. In contrast, cascades employing non-moving porous structures are in principle scalable to any commercial-relevant level [232] due to their inherent modularity characteristics. Perhaps a compromise between efficiency and simplicity in operation combined with scalability is necessary at the stage of commercial-level scale-up decision.

6.3. Isothermal vs. non-isothermal thermochemical cycles

Thermal reduction requires high temperatures and low oxygen partial pressures, whereas oxidation is favored by lower temperatures and high partial pressures of either H_2O or CO_2 . However, the reaction kinetics needs to be considered, which imposes restrictions on the temperature of the water oxidation: if the temperature of this step is too low the reaction becomes too slow and thus inapplicable. To overcome the problems associated with cyclic WS–TR temperature-swing operation mentioned above, the hercynite reaction scheme has been also proposed by the research group of University of Colorado [233] in conjunction with an isothermal two-step process. Since both the forward and the reverse reaction can take place at the same temperature [234] the heat recuperation issue can be thus avoided. By performing both reactions (13) and (14) at 1623 K they demonstrated that hercynite can split water in a two-step isothermal cycle with much higher H_2 yield than a ceria redox cycle performed between 1623 K (TR) and 1273 K (WS). Thus the need for temperature swings and consequent reduced efficiency can be avoided. A little later an isothermal cycle was proposed for the ceria system at 1773 K from the group of Caltech [223]. However, isothermal cycles in a real-scale solar reactor will face the problem of the spatial competition between oxidation and reduction. It seems unavoidable that at some regions of the reactor at least local oxygen evolution will co-exist with hydrogen one. As a matter of fact this phenomenon has been already experimentally observed, but was attributed to other possible causes [223]. This at the best

case can reduce the efficiency/product yield of the process due to re-combination, and at the worst case could lead to explosive mixtures. Actually, this concept has been recently challenged also on the ground of thermodynamic calculations for the case of water splitting by the SNL group. In their study it is argued that isothermal H_2 production is impractical and inefficient, irrespective of reactor design or reactive oxide properties. Instead, an optimal temperature difference between cycle steps, for which efficiency is the highest, can be determined for a wide range of other operating parameters. The group advocates for a combination of well-targeted pressure and temperature swing, rather than either individually, as the most efficient mode of operation of a two-step thermochemical cycle for solar fuel production [235].

7. Conclusions

The work over the last 30 years on solar-aided, redox-pair-based thermochemical cycles exploited initially for hydrogen and currently for syngas and solar fuels production has been presented. In conclusion it can be said that even though thermodynamic and process efficiency studies have shown that such cycles meet the metric of potential viability compared to "benchmark" technologies like electrolysis powered by solar electricity, it is clear that further research efforts are needed for the achievement of these targets in practice. It can be stated that the two main research tasks are in one hand the improvement of solar interfaces and integrated heat recovery schemes and in the other hand solving the main materials-related issues and providing the right functional materials at reasonable costs.

In this perspective it should be borne in mind that "technically simpler" concepts are in principle more attractive for large-scale implementation and demonstration of any technology and in most cases a "trade-off" has to be made between theoretical targets and operation simplicity. Within this framework, perhaps "open-loop thermochemical cycles" where the thermal reduction step is complemented by a "chemical-reduction" one via carbon-containing species can be a viable process option for at least a transition period before syngas produced only by renewable resources. Such cycles exploit similar materials as well as solar concentration technologies; however they can be performed under much milder conditions.

Solutions to those tasks will decisively help solar thermal processes to achieve the role of significantly contributors through carbon-lean to eventually carbon-free and sustainable hydrogen and syngas production on large scale, using only solar energy, carbon dioxide and water as clean and abundant sources for those fuels.

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